



# ***JPRS Report***

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# Science & Technology

## USSR: Chemistry

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UDC 551.510.42

**Size Distribution of Aerosol Particles in Various  
Types of Coastal Air Masses**

*18410179a Tbilisi SOOBASHCHENIYA AKADEMII  
NAUK GRUZINSKOY SSR in Russian  
Vol 131 No 3, Sep 89 pp 517-521*

[Article by G. A. Mestiashvili]

[Abstract] A study is made of the distribution of aerosol particles by size in the littoral zone of the ocean for continental and marine aerosols both in a stable air mass and in a changing air mass (moving onshore and offshore). These variations in air mass were used to generate statistical sets of measured spectral transparencies and to determine the mean values of certain meteorological parameters for these groups. The data confirm the influence of movement of air masses on formation of optical and microphysical characteristics of the atmospheric aerosol in the littoral zone. Figures 2; references 9: 7 Russian, 2 Western.

UDC 543.08:389.0

**Ensuring Reliability of Information Needed for Establishing and Using Chromatographic Retention Data Bases***18410151a Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 44 No 2, Feb 89 (manuscript received 24 Jul 87) pp 221-224*

[Article by A. B. Shayevich, Urals Forest Technology Institute, Sverdlovsk]

[Abstract] The use of preanalyzed, i.e., handbook data, on chromatographic retention is one of the fundamental sources for the identification of substances. Unfortunately, the effectiveness of this source is frequently limited owing to significant discrepancies in the data listed in various publications. Another complication is the frequently occurring single unsupported source of information. Formal acceptance of data contained in any single source can only be considered temporary since handbook data must be reliable. The availability of reliable handbook data is especially critical in connection with establishing data banks needed for chromatographic analysis because of the danger of using only nominally reliable information that may nevertheless be supported by the authority of some other data bank. Ensuring the reliability of this information is a methodologically complex problem, and its solution must include such factors as a well-founded set of tolerance levels for each data group, carefully planned experimentation, qualified critique of analysis results focusing primarily on unobserved systematic errors, and a metrologically correct approach excluding errors that may arise during the stage in which the reference data are used. References 12: 11 Russian, 1 Western.

UDC 543.5.088.8

**Laminar Methods of Analysis of Irradiated Samples***18410151c Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 44 No 2, Feb 89 (manuscript received 14 Dec 87) pp 278-283*

[Article by V. A. Ryzhkov and A. N. Oblivantsev, Nuclear Physics SRI at Tomsk Polytechnical Institute]

[Abstract] The profile of radionuclide distribution in irradiated samples is frequently determined by employing a laminar analytical technique in which the sample is successively treated in a pickling solution and the thickness and radioactivity of each pickled layer is recorded. A major problem of this method lies in determining the correct thickness or depth of analysis. Monitoring the mass of the sample gravimetrically is not always feasible owing to the sensitivity limitations of an analytical balance and the time required. A new method is proposed in which the total activities of the sample and the pickling solution are continuously monitored and the thickness of the etched layer is determined by the

drop in detector load resulting from the transfer of activity from the sample to the solution. During this transfer of activity, the measuring geometry changes from that of a flat or two-dimensional source (the sample) to a bulk volume three-dimensional source (the solution). The greater the discrepancy in effectiveness of recording  $\gamma$ -radiation between a two-dimensional and three-dimensional source, the more significant the drop in detector load during the pickling process, and the more accurate the control of pickling depth becomes. In the present work several rapid methods are proposed for such laminar activation analysis that are based on continuous pickling of irradiated samples and simultaneous control of the change in  $\gamma$ -activity of the radionuclide in the sample-pickling solution system or by the change in optical density of the solution. Some results are presented on the laminar analysis of LiF samples irradiated with protons (5 Mev) and  $N^{14}$  ions (16 Mev); these indicate that the time could be reduced to less than 10 minutes, which makes it possible to determine the profiles of short-life radionuclides such as  $N^{13}$ ,  $O^{15}$ , and  $C^{11}$ . Figures 3; references 10: 9 Russian, 1 Western.

UDC 543.3:628.1

**Determining Zinc in Natural Waters Using Reagent Test Paper RIB FMOPF-6-Ts***18410151d Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 44 No 2, Feb 89 (manuscript received 3 Dec 87) pp 289-291*

[Article by T. V. Lifintseva, Ye. A. Stradomoskaya, V. M. Ostrovskaya, M. S. Aksenova, V. A. Kimstach, K. N. Dasarov, and L. V. Boyeva, Rostov State University imeni M. A. Suslov, Chemical Reagents and Ultrapure Chemical Substances SRI (A-U), Moscow, Hydrochemistry Institute, Rostov-on-Don]

[Abstract] To maintain operational control of environmental pollution, particularly ground waters, it has become necessary to develop rapid and sensitive field methods for determining heavy metals. Such methods have been successfully developed for copper in various waters by employing the test papers RIB FMOPF-6-Ts and RIB FMMOPF-6-Ts with covalently fixed chromogenic reagents. In the present work it was demonstrated that the title test paper can be used, and a rapid semi-quantitative method was developed for determining zinc to 10 microns per liter of water in 3-10 minutes. Test results compared favorably with atomic absorption and photometric methods using a variety of river water samples. Figures 3; references 6 (Russian).

UDC 543.7:543.244.6

**Determination of Yttrium, Copper, and Barium in Oxide  $YBa_2Cu_3O_{9-x}$** *18410151e Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 44 No 2, Feb 89 (manuscript received 22 Dec 87) pp 307-310*

[Article by I. M. Novoselova and I. V. Moroz, Ural Chemistry SRI, Sverdlovsk]

[Abstract] Interest in the title oxides focuses on their superconductor properties under certain conditions and possible electronics applications. Correct stoichiometric compositions are required in preparing charges or solutions for the preparation of these oxides. Toward this end, it has become necessary to develop simple and dependable methods for determining Y, Ba, and Cu. Published methods for determining Ba and Cu require preliminary separation. Either Ba is precipitated out, or else the Cu is extracted. The Y is then precipitated with excess  $\text{NH}_3$  as hydroxide. These methods are tedious and time-consuming and could result in the loss of certain components by coprecipitation. In the present work methods based on successive complexometric titrations were developed for determining Y, Ba, and Cu in milligram quantities of the title oxide systems that do not require preliminary separation of the components. Standard deviation of test results obtained for an artificially prepared mixture and a model solution does not exceed 0.04 percent. References 10 (Russian).

UDC 546.21.06:538.945:666.3

#### Determination of Oxygen Bound With Copper in Ceramic High-Temperature Superconductors

18410151f Moscow *ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 44 No 2, Feb 89 (manuscript received 24 Nov 87) pp 324-327*

[Article by V. P. Seminozhenko, Z. M. Nartova, N. I. Shevtsov, A. B. Blank, L. I. Afanasiadi, R. Yu. Itskovich, and L. A. Kvichko, Monokristallreaktiv Scientific Production Association, Kharkov]

[Abstract] Aside from structural factors, oxygen content has a decisive effect on the properties of ceramic high-temperature superconductors. It has been demonstrated that in an orthorhombic ceramic having the structure  $\text{YBa}_2\text{Cu}_3\text{O}_x$ , the transition temperature  $T_c$  changes from 92K to 28K as  $x$  decreases from 7.0 to 6.3. The variation in oxygen content is due to the variable valence of copper. Various methods of neutron activation and microsound, thermogravimetry in air or oxygen, or even reduction in an argon-hydrogen atmosphere are used to determine oxygen in these materials. However, these methods have relative errors ranging from 4 to 10 percent, which precludes using published methods for optimizing high-temperature ceramic superconductors since a 1-1.5 percent change in the oxygen content results in a 10-15 K change in  $T_c$ . Oxygen that is bound to copper could be also be determined by the loss in weight after reduction with hydrogen. In the present work this method was used to determine oxygen in ceramics having the general formula  $\text{LnR}_2\text{Cu}_3\text{O}_x$ , where Ln and R are one or a combination of rare earth elements and alkaline earth elements, respectively. The relative standard deviation or error for determining oxygen was  $(6-9) \cdot 10^{-3}$ . Figure 1; references 12: 5 Russian, 7 Western.

UDC 543.422.002.5:546.215

#### The Flow-Through Injection Analysis. Spectrophotometric Determination of Hydrogen Peroxide in Atmospheric Precipitation Using Peroxidase

18410151g Moscow *ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 44 No 2, Feb 89 (manuscript received 30 Dec 87) pp 341-345*

[Article by I. D. Yeremina, L. K. Shpigun, and Yu. A. Zolotov, Moscow State University imeni M. V. Lomonosova; Geochemistry and Analytical Chemistry Institute imeni V. I. Vernadskiy, Moscow]

[Abstract] Sulfate ions are formed in the atmosphere by the oxidation of  $\text{HSO}_3$  with hydrogen peroxide, and in order to study the formation and removal of sulfur compounds from the atmosphere it becomes necessary to have a means of monitoring the hydrogen peroxide concentration in atmospheric precipitations. In the present work a flow-through injection technique was developed in which hydrogen peroxide can be determined within the range of 0.1-10 micromoles. The method is based on the enzymatic reaction of 2,2'-azinodi(3-ethylbenzthiazolin-6-sulfonate with hydrogen peroxide in the presence of peroxidase catalyst extracted from horseradish. The reaction is carried out in a FIA-star-5020 flow-through injection analyzer (Tekator, Sweden) using a FIA-5023 spectrophotometer. Figures 5; references 9: 1 Russian, 8 Western.

UDC 543.422.8

#### X-Ray Radiometric Determination of Cobalt in Iron-Manganese Ocean Floor Nodules

18410151h Moscow *ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 44 No 2, Feb 89 (manuscript received 3 Dec 87) pp 351-355*

[Article by V. V. Ivanenko, V. N. Kustov, A. Yu. Metelev, and K. A. Rakita, Chemistry Institute, Vladivostok]

[Abstract] The multielement X-ray radiometric method of analysis using radionuclide sources and transistorized detectors has found broad applications in studying the element composition of various minerals and ecological research. Less known are the possibilities of this method for studying ocean floor nodules, one of the most promising minerals. Work in this direction proceeded by using the saturated layer technique with various methods for eliminating matrix effects. One feature of these nodules is the predominant Mn and Fe content (30-40 percent), which markedly complicates the determination of cobalt, one of the most industrially important components of the nodules. The weak intensity of the  $K_\alpha$  line of Co is overshadowed by the  $K_\beta$  lines of Mn and Fe. In the present work this was overcome by using a thin-layer technique that is less affected by matrix effects. The method was used on board ship to determine the content



of cobalt and other elements in iron-manganese nodules from the Pacific Ocean floor. Figures 4; references 10: 8 Russian, 2 Western.

UDC 634.0.813.2:647.013.21

#### Silver Birch Bark Leucoanthocyanidins

18410162D Novosibirsk IZVESTIYA SIBIRSKOGO OTDELENIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKIKH NAUK in Russian No 1 Jan 89 (manuscript received 17 Mar 87) pp 86-90

[Article by S. M. Bondarenko, S. Ya. Dolgodvorova, G. N. Chernyayeva, Institute of Forestry and Wood Products imeni V. N. Sukachev, Siberian Division, USSR Academy of Sciences, Krasnoyarsk]

[Abstract] Continuing studies of the phenol substances in the bark of the silver birch *betula pendula* Roth, the authors studied the leucoanthocyanidin (LA). This article presents the results of determination of the quantitative content of LA, the influence of growth conditions on content and data for identification. The results indicate that the basic leucoanthocyanidins in birch bark are leucodelphinidine (5,7,3',4',5'-pentaoxyflavan-3,4-diol), leucopetunidine (3'-methoxy-5,7,4',5'-tetraoxyflavan-3,4-diol) and leucocyanidine (5,7,3',4'-tetraoxyflavan-3,4-diol). Figure 1; References 25: 13 Russian, 12 Western.

UDC 543.43:546.24:546.28

#### Extraction-Spectrometric Method of Determining Silicon in Highly Pure Substances. I. Determination of silicon in tellurium

18410162E Novosibirsk IZVESTIYA SIBIRSKOGO OTDELENIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKIKH NAUK in Russian No 1 Jan 89 (manuscript received 7 Jul 87) pp 101-04

[Article by V. P. Shaburova, I. G. Yudelevich, Institute of Heteroorganic Chemistry, Siberian Division, USSR Academy of Sciences, Novosibirsk]

[Abstract] The purpose of this work was to develop a method of determining silicon in cadmium, mercury, tellurium and  $Cd_xHg_{1-x}Te$  (cmt). This article discusses determination of silicon in tellurium by a spectrophotometric method utilizing malachite green. The method is based on extraction separation of the base with TBP, formation of an ionic silicon-molybdenum polyacid-malachite green ionic associate and subsequent measurement of the optical density of the solution on the spectrophotometer. The method can be used to determine  $2 \times 10^{-1}$ - $3.10^{-4}\%$  Si. Figures 3; References 8: Russian.

UDC 542.61:543.43:546.48:546.28

#### Extraction-Spectrometric Method of Determining Silicon in High-Purity Substances. II. Determination of Silicon in Cadmium

18410162F Novosibirsk IZVESTIYA SIBIRSKOGO OTDELENIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKIKH NAUK in Russian No 1 Jan 89 (manuscript received 7 Jul 87) pp 105-109

[Article by I. G. Yudelevich, V. P. Shaburova, L. V. Shamrina, Institute of Heteroorganic Chemistry, Siberian Division, USSR Academy of Sciences, Novosibirsk]

[Abstract] A spectrophotometric method has been developed for determining silicon in tellurium at a minimum concentration of  $3.2 \times 10^{-4}\%$  Si. This article reports on development of a method of determining Si in Cd by a spectrophotometric method based on formation of an ionic associate of silicomolybdenum heteropolyacid with malachite green. The limit of detection is  $3.9 \times 10^{-4}\%$  of the initial cadmium charge and  $7.8 \times 10^{-5}\%$  of 0.5g cadmium chloride. The relative standard deviation  $S_r=0.07-0.13$ . Figure 1; References 9: 7 Russian, 2 Western.

UDC 549.3+546.59+542.61

#### Dissolution of Gold in Cyanide Solution in Contact with Sulfide Minerals I. Galvanic Element Gold-Pyrite-Sodium Cyanide Solution

18410162G Novosibirsk IZVESTIYA SIBIRSKOGO OTDELENIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKIKH NAUK in Russian No 1 Jan 89 (manuscript received 19 May 87) pp 129-34

[Article by V. I. Varentsova, V. K. Varentsov, V. O. Lukyanov, Institute of Solid-state Chemistry and Processing of Mineral Raw Materials, Siberian Division, USSR Academy of Sciences, Novosibirsk]

[Abstract] A study is made of the influence of certain factors on the functioning of a gold-pyrite-sodium cyanide solution shorted electrochemical system. Dissolution of gold in contact with pyrite was studied in the physical system and on a model. The physical system was made of plates of gold and pyrite in direct contact in a glass clamp. The model was a galvanic element with metallic gold foil or wire electrodes and a mineral paste pyrite electrode. The studies showed that the electrochemical characteristics of the system depend essentially on the ratio of surfaces of gold and pyrite and on the properties of the electrolyte. In cyanide leaching of gold-containing intermediate products with low ratio of gold to sulfide, the dissolution of gold will be determined by the electrode potential of the pyrite. Leaching of gold is performed under these conditions at potentials which do not provide the maximum possible process rate. Varying the solution composition can accelerate the process of gold dissolution. Other methods of intensifying the process should also be sought. Figures 4; References 11: 10 Russian, 1 Western.

UDC 541.141.7:621.373.826

**Isotopically Selective Dissociation of  $\text{CF}_3\text{I}$  Due to Changes in Specific Pressure and Isotopic Concentration**

18410165b Moscow *KHIMICHESKAYA FIZIKA* in Russian Vol 8 No 3, Mar 89 (manuscript received 31 Mar 88) pp 323-332

[Article by V. B. Laptev and N. P. Furzikov, Institute of Spectroscopy, USSR Academy of Sciences, Troitsk]

[Abstract] The goal of this work was to experimentally and theoretically study the effect of an excited rare isotope concentration  $^{13}\text{CF}_3\text{I}$ , on the yield and selectivity of multiphoton dissociation (MPD) in a wide range of specific pressure changes of the dissociating gas. A model developed earlier was used to interpret the experimental data. This model considered the heterogeneity of the laser field interaction with rotational and vibrational states. It was concluded that at a low concentration of this rare isotope the sharp drop in MPD selectivity with certain specific pressure was due to a rapid increase in the yield of the molecular dissociation of the nonresonating, rich isotope, which was caused by its vibrational self-heating. This process develops because of the uneven interaction of the exciting radiation with the initial vibrational distribution of the rich isotope molecules. When the concentration of the rare isotope is increased, the lowered dissociation selectivity is also connected with an increased yield of MPD molecules of rich isotope that become excited due to V-V-exchange with vibrationally "hot" molecules of the resonating rare isotope. Figures 2; references 27: 15 Russian, 12 Western (2 by Russian authors).

UDC 541.144.8 + 541.121.123

**Effect of Quartz Surfaces on Photochemical Exchange Processes in Pulse Photolysis of Lead Dibromide Vapors**

18410165c Moscow *KHIMICHESKAYA FIZIKA* in Russian Vol 8 No 3, Mar 89 (manuscript received 18 Jan 88) pp 333-342

[Article by Ya. E. Rupkus, A. P. Ubelis, and E. K. Kraulina, Latvian State University imeni P. Stuchka, Riga]

[Abstract] Systematic studies of photochemical reactions by the pulse photolytic method led to the conclusion that, during extended heating of  $\text{PhX}_2$  in a quartz vessel, the molecular composition of its vapor within this vessel was undergoing qualitative changes. To explain this, it was hypothesized that a heterogeneous thermal disproportionation reaction of  $\text{PbX}_2$  took place with the formation of a gaseous and a solid product. The gaseous product filled the vessel, and the solid bonded chemically with the quartz walls. This indicated that there are possibly two channels for electron excitation of the reaction

products. The relationship between the processes occurring during pulse photolysis of  $\text{PbBr}_2$  was studied by the spectroscopic method. Illumination of the reaction vessel with a continuous pulse of the lamp resulted in photolysis of both reaction products; the dibromide vapor and solid lead tetrabromide and photodecomposition of lead atoms at the quartz surface. It was shown that the total vapor pressure of both components expressed as a function of the temperature of the solid phase of dibromide differed significantly from that calculated by the Clausius-Clapeyron equation for bivalent salts. Figures 4; references 25: 10 Russian, 15 Western (1 by Russian author).

UDC 621.378.33

**Absorption of  $\lambda = 28 \mu\text{m}$  Irradiation in Water Vapor After a Shock Wave**

18410165e Moscow *KHIMICHESKAYA FIZIKA* in Russian Vol 8 No 3, Mar 89 (manuscript received 9 Mar 88) pp 406-412

[Article by A. B. Britan, V. A. Levin, V. A. Sorokin, A. M. Starik, and A. N. Khmelevskiy, Institute of Mechanics, Moscow State University imeni M. V. Lomonosov]

[Abstract] The absorption coefficient of  $28 \mu\text{m}$  radiation by water vapor was determined and compared with theoretically calculated  $K_v$  values for flow parameters behind shock waves providing an impact-type mechanism of the expansion of spectral lines. It was shown that the functions  $K_v(T)$  and  $K_v(P)$  can be described on the basis of a phenomenological theory of absorption by using the Einstein coefficient  $A_{mn} = 2 \text{ s}^{-1}$  for the transition  $020(5_{50})$  approaches  $001(6_{33})$  along with the impact width of spectral line  $\lambda_{020}$  approaches  $001 = 0.45 \text{ cm}^{-1} \text{ atm}^{-1}$ . The values  $A_{mn}$  and  $\gamma_s^{020}$  approaches  $001$  can be recommended for utilization in respective calculations. The  $\gamma_s^0$  values for purely rotational transitions range from 0.6 to  $0.8 \text{ cm}^{-1} \text{ atm}^{-1}$ . Figures 3; references 27: 11 Russian, 16 Western.

UDC 541.13 + 539.196.5

**Change in Vibrational Distribution of CO Molecules in Carbon Sulfide Flames Under Influence of Chemical CO-Laser Irradiation**

18410165f Moscow *KHIMICHESKAYA FIZIKA* in Russian Vol 8 No 3, Mar 89 (manuscript received 22 Mar 88) pp 413-418

[Article by V. A. Dudkin, Institute of Mechanics Problems, USSR Academy of Sciences, Moscow]

[Abstract] Population changes in vibrational-excited levels of CO molecules that form during the combustion of carbon sulfide were studied as they were affected by chemical CO-laser irradiation in the vibrational transition range from 13-12 to 7-6. In such a system, the time required for the formation of a new quasistationary state

depends on the number of vibrational levels interacting with the field and can exceed the time characteristics of the processes of induced emission and desorption of quanta in a dual-level system. The data obtained could serve as a starting point for concurrently considering the effect of collision and irradiation on the distribution of CO molecules formed during a chemical reaction, estimating characteristic times of its changes at given intensities in the spectrum of laser radiation, and calculating the changes in the energy reserves in the system. Figures 3; references: 8 (Russian, 1 by Western authors).

UDC 543.42:538.945

### Microscopic Probe Method in Studies of High-Temperature Superconducting Materials

18410165g Moscow *KHIMICHESKAYA FIZIKA* in Russian Vol 8 No 3, Mar 89 (manuscript received 14 Jan 88) pp 423-424

[Article by V. I. Krinichnyy, O. Ya. Grinberg, G. I. Kozub, and Ya. S. Lebedev, Institute of Chemical Physics, USSR Academy of Sciences, Moscow]

[Abstract] "Spot" paramagnetic samples placed in an EPR spectrometer resonator together with test samples were used to determine the magnetic characteristics of high-temperature superconductors (HTSC). HTSC placed next to a paramagnetic sample could lead to altered local magnetic fields affecting the probe. Changes in the form and positioning of the EPR line could be used to determine the value of a local field at the point where the paramagnetic sample was placed, thus acting as a macroscopic spin probe. Indeed, this proved to be a very effective method in studying HTSC, especially in studying the heterogeneity of the sample's structure. This method makes it possible to determine the magnetic moment and magnetic susceptibility of a sample portion of an extended superconductive sample. References 5: 3 Russian, 2 Western.

UDC 541.714

### Photochemical Reactions in Ethanol Solutions of Triphenylene at 77 K

18410165h Moscow *KHIMICHESKAYA FIZIKA* in Russian Vol 8 No 3, Mar 89 (manuscript received 27 Apr 88) pp 425-427

[Article by V. V. Akhlypin and V. D. Shatrov, Scientific Research Institute of Intermediary Organic Products and Dyes, Moscow]

[Abstract] In a previous paper it was shown that, during the photolysis of triphenylene (TP) in ethanol, the principal radical product is its "adherence" radical IH-TP, which reaches an absorption maximum at 410.5 nm. In the present work the mechanism of the formation of IH-TP. was studied by using UV spectroscopy. This radical formed by the sequential transfer of an electron from the ethanol molecule to an excited TP molecule,

followed by the transfer of a proton from the ethanol cation radical OH group to the TP anion radical. Thus, formation of the excited complex with  $e^-$  transfer may be one of the possible routes of the destruction of a TP molecule in alcohol solutions irradiated with near-ultraviolet light. Figure 1; references 11: 7 Russian, 4 Western.

UDC 541.034:541.122.4:541.183:549.67

### Study of Equilibrium Adsorption of Binary $H_2$ - $D_2$ Mixture on NaX Zeolite at High Presures

18410168a Moscow *IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA* in Russian No 3, Mar 89 (manuscript received 26 Oct 87) pp 509-515

[Article by M. A. Luvyn, T. S. Yakubov, M. B. Gorbunov, V. A. Gorlov, A. P. Gay, V. V. Serpinskiy, Institute of Physical Chemistry, USSR Academy of Sciences, Moscow]

[Abstract] Experiments are conducted on the adsorption of mixtures of stable isotopes of hydrogen in a previously unstudied range of temperatures (100-300 K), pressures (0.1-7 MPa) and compositions. A method is suggested for processing the experimental data (with allowances made for the nonideal nature of the gas phase) by means of a thermal adsorption equation. The parameters of the equation are determined. The variation of separation coefficient with adsorption equilibrium parameters is determined, and it is found that the separation coefficient is independent of total gas mixture pressure in the selected interval of the parameters and stops depending on gas phase composition as temperature rises. It is shown that the ideal solution theory is not applicable. Figures 3; References 11: 9 Russian, 2 Western.

UDC 541.183:541.122.4:549.67

### Calculation of Adsorption Equilibrium Parameters of Inert Gases and Their Binary Mixtures on NaX Zeolite

18410168b Moscow *IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA* No 3 Mar 89 (manuscript received 3 Sep 87) pp 515-519

[Article by L. A. Vashchenko, V. V. Katalnikova, V. V. Serpinskiy, Physical-Technical Institute of Low Temperatures, Ukrainian Academy of Sciences, Kharkov; Institute of Physical Chemistry, USSR Academy of Sciences, Moscow]

[Abstract] There are no universal methods for computing the parameters of adsorption equilibrium, though some methods suggested in the literature can be used for such calculations. One such method is the quasichemical adsorption model. The model of adsorption of a gas by zeolites is studied from the standpoint of classical thermodynamics. Adsorption isotherm equations are derived by computing the thermodynamic equilibrium

constants of the heterogeneous gas-solid reaction. Three molecular models are used to generate partial adsorption isotherms: localized adsorption without interaction, localized adsorption with interaction, and nonlocalized adsorption. The adsorption isotherms of krypton, xenon and nitrogen are computed in the 140-270 K temperature interval at pressures of 0.3 Pa to 65 kPa. The limit of applicability of the model is determined. Equilibrium diagrams of adsorption krypton-xenon solutions are constructed for 170 and 220 K. Figures 2; References 7: 3 Russian, 4 Western.

UDC 543.257.1:661.185.1

#### Assessment of Neonol-AF<sub>5</sub>-5-Ba-Tetraphenylborate Complexes as Membrane Electrodes

18410174a Moscow *ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 44 No 3, Mar 89 (manuscript received 23 Feb 88) pp 408-412*

[Article by R. K. Chernova, Ye. G. Kulapina, Ye. A. Materova, and Ye. V. Tretyachenko, Saratov State University imeni N. G. Chernyshevskiy]

[Abstract] Trials were conducted with neonol-AF<sub>5</sub>-5-Ba-tetraphenylborate (NBPB) membranes to assess their utility as electrode components in the determination of nonionic surfactants (NS). Studies with a series of neonols (C<sub>9</sub>H<sub>19</sub>C<sub>6</sub>H<sub>4</sub>O-(C<sub>2</sub>H<sub>4</sub>O)<sub>n</sub>H, n = 5, 6, 9, or 12) yielded E vs. log<sub>[NS]</sub> plots on which the emf was linearly dependent on log<sub>[NS]</sub> in the 10<sup>-3</sup> to 10<sup>-2</sup> M interval, with a slope of 27-29 mV/p[NS]. The attainment of a stable potential required 30-40 min with 10<sup>-6</sup> to 10<sup>-5</sup> M solutions, and 10-15 min with 10<sup>-4</sup> to 10<sup>-2</sup> M solutions, with the electrodes showing a useful shelf-life of 3-4 months. The use of the NBPB complexes for potentiometric titration of neonols and other NS displayed a sharp jump of about 150 mV for 10<sup>-3</sup> M solutions and a change of about 40 mV for 10<sup>-6</sup> M solutions. Application of this system to the analysis of total NS in waste waters and comparison of the results with the data provided by photometric analysis yielded excellent agreement, with s<sub>r</sub> ranging from 0.02 to 0.04. Figures 4; references 14: 5 Russian, 1 Chinese, 8 Western.

UDC 543:546.9

#### Sorption-Luminescence Analysis of Osmium in the Phase of Silica Chemically Modified With Sulfonic Groups

18410174c Moscow *ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 44 No 3, Mar 89 (manuscript received 18 Jan 88) pp 461-466*

[Article by I. R. Zmiyevskaya, V. I. Fadeyeva, T. I. Tikhomirova, A. Yu. Stakheyev, and G. V. Kudryavtsev, Moscow State University imeni M. V. Lomonosov]

[Abstract] A highly sensitive method was developed for the analysis of osmium based on the formation of the luminescent complex tris(1,10-phenanthroline)osmium(II). The extraction step consisted of the osmium(VIII) sample, 1,10-phenanthroline, and hydrazine as the reducing agent, with pH adjusted either with HCl or NaOH, with concomitant adsorption to sulfonic acid-modified silica. Analysis of luminescence (approximately 720 nm) data showed that optimum conditions for complex formation consisted of pH 6-7, a temperature of 98 plus or minus 2°C, Os:phenanthroline ratio of 1:2 x 10<sup>3</sup>, and 5 x 10<sup>-3</sup> M hydrazine. Formation of the complex on the surface of the modified silica occurs in 30 min, whereas in solution the time required is 3 to 4 hours. Standard curves for the solid phase were linear in the 0.5-5 >mg osmium range, with a detection limit of 2 x 10<sup>-5</sup>% (or 1 x 10<sup>-3</sup> µg/ml in a final volume of 20 ml and 0.1 gm silica). Figures 4; references 9: 6 Russian, 3 Western.

UDC 543.43:546.719

#### Differential Spectrophotometry in Kinetic Determination of Rhenium

18410174d Moscow *ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 44 No 3, Mar 89 (manuscript received 21 Oct 87) pp 565-567*

[Article by V. I. Lazareva and A. I. Lazarev, Institute of Novel Chemical Problems, USSR Academy of Sciences, Chernogolovka]

[Abstract] Differential spectrophotometry has been employed for a kinetic method of rhenium analysis, using colored glass filters in lieu of reference solutions. The system was based on the redox reactions occurring between tellurium and lead (II), catalyzed by rhenium in the solution. In this case the linear relationship between the optical density at 400 nm was monitored for 60 min. The effective molar extinction coefficient was 1.6 x 10<sup>7</sup> over the period of observation. Reproducibility for the differential spectrophotometric method was s<sub>r</sub> is less than or equal to 0.01, and for direct spectrophotometry s<sub>r</sub> is less than or equal to 0.07. References 5: 4 Russian, 1 Western.

UDC 543.42

#### Ultrasonic Extraction of Trace Elements From Soils and Plants for Subsequent Determination by Atomic Absorption and Atomic Emission Spectrometries

18410174e Moscow *ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 44 No 3, Mar 89 (manuscript received 18 Nov 87) pp 567-570*

[Article by D. M. Kumina, Ye. N. Savinova, T. V. Shumskaya, M. D. Alybayeva, and A. V. Karyakin, Institute of Geochemistry and Analytical Chemistry imeni V. I. Vernadskiy, USSR Academy of Sciences, Moscow]

[Abstract] Further development was conducted on the use of sonication for extraction of trace elements from various soil and plant samples for subsequent analysis by atomic absorption and emission spectrometries. The 2-5 gm samples were dried at 105°C to constant weight, homogenized, and treated with 0.5 ml mixture (3:1) of HCl and HNO<sub>3</sub> in 4.5 ml water. They were then exposed to ultrasound (0.6 A, 44 kHz) for 4 min. The residue was permitted to settle for 15 min and then filtered, with the sediment subjected to two

more repetitions of the ultrasonication procedures. The method was found to yield suitable samples for analysis by atomic absorption and emission spectrometries and was shown to be applicable to Cu, Zn, Co, Ni, and Mn. Excellent agreement was obtained with State standard samples and with samples prepared for analysis by ashing, with a standard deviation of 0.12. Thus, the extraction of certain trace elements by ultrasonication appears to be a method with universal applicability. References 3: 2 Russian, 1 Western.

UDC 541.128.13

**Catalytic Properties of Palladium Applied to Oxides of Different Chemical Natures in Hydrogenation of CO**

18410155D Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 55 No 2, Feb 89 (manuscript received 1 Dec 87) pp 151-157

[Article by Yu. I. Pyatnitskiy, T. M. Shapinskaya, V. P. Stasevich, G. V. Filonenko, V. L. Struzhko, V. I. Gritsenko, and G. G. Girushtin, Institute of Physical Chemistry, Ukrainian Academy of Sciences, Kiev]

[Abstract] Previous studies have revealed great variation in the activity and selectivity of palladium catalysts with the carrier and various modifying additives. Data must be systematically accumulated on the effect of the carrier on palladium's activity and selectivity. This article studies the catalytic properties of palladium catalysts in a glass reactor at atmospheric pressure with a chromatographic analysis of the reaction products. All catalysts studied contained the same quantity of palladium on various carriers: MgO, La<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub>, and SiO<sub>2</sub> modified with ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. The results indicate a wide variation in the catalytic properties of palladium on different carriers, with the mechanism causing the variation to differ for different carriers. The results, which are presented in tabular form, can be used to interpret data obtained on catalysts on various carriers. Figures 2; References 17: 7 Russian, 10 Western.

UDC 541.183

**Calculation of Equilibrium Constants of Competing Adsorption of Micro-Macro Components on Zeolites From Data on Individual Adsorptives**

18410161b Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: SERIYA 2, KHIMIYA in Russian Vol 30, No 1, (manuscript received 21 Oct 87) pp 32-35

[Article by T. A. Kuznetsov, I. Ye. Ovcharenko, A. Ye. Sigayeva, and A. M. Tolmachev, Chair of Physical Chemistry]

[Abstract] In a previous work it was demonstrated that the equilibrium constants in an adsorption competing mixture of micro and macro components on a microporous adsorbent may be computed for an ideal gas mixture based on a given formula. In the present work it is demonstrated that the same constants may be computed from the Henry constant data for individual adsorptives and the adsorption isotherm of any other substance on the zeolite, thus making it possible to lessen the volume of experimental work in searching for optimally selective adsorbents. Figure 1; references 8 (Russian).

UDC 541.128

**Catalase Activity of Mixed Pt-Pd Adsorption Catalysts**

18410161d Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: SERIYA 2, KHIMIYA in Russian Vol 30 No 1, Jan-Feb 89 (manuscript received 28 Aug 87) pp 63-67

[Article by V. I. Shekhobalova and L. V. Voronova, Chair of Physical Chemistry]

[Abstract] Carrier-based mixed catalysts present both practical and theoretical interest, and many references indicate that small additions of a second component to a base catalyst frequently provides a marked increase in productivity of the catalyst, while a change in activity with a change in catalyst composition may be helpful in explaining both the nature of catalytically active sites and the reaction mechanism itself. In the present work a study is made of mixed Pt-Pd adsorption catalysts on a silica gel carrier. Both metals are used as catalysts in hydrogen peroxide decomposition, although the activity of palladium is much lower than that of either platinum black or very small (0.5 percent) amounts of platinum adsorbed on a carrier. To study their combined action, three series of mixed catalysts were prepared that contained 3 percent by weight Pt on silica gels having respective surface areas of 345, 88, and 28 square meters per gram and also containing 0.5 to 9.0 percent by weight Pd. Data collected for all series included the activity, kinetics, and surface areas of active metals and data from an x-ray analysis of Pt and Pd for the first series. A 0.8 reaction order was maintained in all cases. The reaction rate constants changed markedly between 0 and 9 percent by weight of Pd, the initial additions of palladium to 0.5 percent having the greatest effect. From 0.5 to 1.0 percent there was a sharp drop in activity, similar to that observed in most two-component catalyst systems. The results indicate that the addition of small amounts of other components is a promising way to increase the productivity of catalyst systems. Figure 1; references 9 (Russian).

UDC 541.15

**Fragmentation and Ion-Molecular Reactions of Isooctane (2,2,4-Trimethylpentane) Cation-Radical**

18410161e Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: SERIYA 2, KHIMIYA in Russian Vol 30 No 1, Jan 89 (manuscript received 21 Jul 87) pp 74-78

[Article by Ye. A. Antonova and T. F. Troshchilova, Chair of Electrochemistry]

[Abstract] Sufficient experimental evidence has now been accumulated to make it possible to assume that dissociation of molecular ions takes place during liquid-phase radiolysis of alkanes and that splinter ions may be looked upon as precursors of end products. However, the



derivation of a fragmentation mechanism from the overall process of hydrocarbon radiolysis still presents experimental difficulties since "chemically" different active particles could combine to form the same end products. For this reason information on the fragmentation and reactivity of molecular ions of alkanes is obtained from experiments in which the hydrocarbon cation-radical is generated by "indirect" ionization in a perhalide matrix. In this case radiolysis products of the matrix are not hydrocarbons, and the perhalide compounds, reacting with electrons, prevent the formation of excited hydrocarbon molecules resulting from substitution of cation-electron neutralization with cation-anion. It has been previously demonstrated that the isooctane molecular ion formed during charge transfer in liquid  $C_6F_6$  and  $CCl_4$  matrices is unstable and that some of the  $C_8H_{18}^+$  cation-radicals are able to dissociate at the C-C bonds to neutralization. The basic end products of dissociative ionization of isooctane in the hexachlorobenzene and tetrachloromethane matrices are methane, isobutane, and isobutylene. In the present work a study was made of the effects of ethanol additions on the end product yields of isooctane molecular ion fragmentation. Mixtures of  $C_6F_6$ -2.4M  $C_8H_{18}$ - $C_2H_5OH$  were irradiated with a  $^{60}Co$  source at 28° C. Methane, isobutane, and isobutylene were analyzed by gas adsorption and gas-liquid chromatography. The results indicate that ethanol has only a weak effect on the radiation-chemical yield of methane and isobutylene, but that the yield of isobutane is cut almost in half at alcohol concentrations of 0.4M and becomes equal to that of methane and isobutylene at 1.2M. Figures 2; references 14: 2 Russian, 12 Western.

UDC 541.6:541.128:546.623-188

#### Formation of Phase Composition and Structure of Cobalt-, Nickel-, and Copper-Containing Oxide Catalysts Based on Activated Aluminum

18410168c Moscow IZVESTIYA AKADEMII NAUK  
SSSR: SERIYA KHIMICHESKAYA in Russian  
No 3, Mar 89 (manuscript received  
18 Nov 87) pp 519-523

[Article by R. B. Akhverdiyev, I. A. Timakov, R. G. Sarmurzina, V. I. Yakerson, M. I. Rustamov, M. K. Guseynova, Sh. K. Seytzhanova, Institute of Organic Chemistry imeni N. D. Zelinskiy, USSR Academy of Sciences, Moscow]

[Abstract] A previous work determined that multicomponent alloys can be reacted with water at room temperature to produce effective deposited catalysts. This original method is used as the basis for production of other catalysts. Results are presented from a study of the phase composition of Co-, Ni- and Cu-containing catalytic systems based on activated aluminum. Aluminum oxide and hydroxide carriers produced through the interaction of aluminum indium and aluminum gallium with water are multiphase systems that contain pseudoboehmite, baeirite, and In, in the first instance, and  $\gamma-Al_2O_3$ ,  $In_2O_3$ ,

and In, in the second. The presence of Co and Ni as an alloy with activated aluminum determines the x-ray amorphous nature of the Co- and Ni-containing phases in all stages, including heat treatment of the oxide and hydroxide systems. Introduction of the Co, Ni and Cu ions to the aluminum oxide or hydroxide matrices produced from activated aluminum has a definite influence on the formation of  $Co_3O_4$ ,  $CoAl_2O_4$ , and  $NiAl_2O_4$  after heat treatment. In the copper-containing catalysts, oxides are formed even before heat treatment. References 5 (Russian).

UDC 541.63:542.941.7:541.65:547.466

#### Synthesis of Optically Active Amino Acids in Asymmetrical Interphase Catalysis

18410168i Moscow IZVESTIYA AKADEMII NAUK  
SSSR: SERIYA KHIMICHESKAYA in Russian  
No 3, Mar 89 (manuscript received  
16 Nov 87) pp 631-635

[Article by Yu. N. Belokon, V. I. Maleyev, T. F. Savelyeva, N. S. Garbalinskaya, M. B. Saporovskaya, V. I. Bakhmutov, V. M. Belikov, Institute of Hetero-Organic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow]

[Abstract] Preliminary data are presented on the alkylation of  $Ni^{2+}$  complexes of the Schiff base of glycine with N-(2-pyridine-carbonyl)-o-aminobenzophenone and a Schiff base of alanine with N-(2-piperidinecarbonyl)-o-aminobenzaldehyde in asymmetrical interphase catalysis, with N-benzyl cinchonidine chloride (NBCC) used as a chiral catalyst. The optical yield is found to depend on the type of complex used and the nature of the alkyl halide. The reaction conditions also influence the optical yield. Figure 1; References 14: 3 Russian, 11 Western.

UDC 542.97:547.284

#### Polycondensation of Ketones, Catalyzed by 12-Phosphorotungstic Acid

18410168n Moscow IZVESTIYA AKADEMII NAUK  
SSSR: SERIYA KHIMICHESKAYA in Russian  
No 3, Mar 89 (manuscript received  
22 Jun 88) pp 731-733

[Article by V. F. Chuvayev, Ye. M. Yaroslavl'tseva, Institute of Physical Chemistry, USSR Academy of Sciences, Moscow]

[Abstract] Previous articles studied the possibility of polymerization and polycondensation of ketones by ordered placement of monomer molecules. In anaerobic polycondensation at 453 K in the presence of compounds such as  $ZnCl_2$  or  $TiCl_4$ , stable polyvinyls have been produced. Condensation of acetone was also observed upon dissolution of certain anhydrous heteropolyacids. The process took place under normal conditions, but distillation of the reaction mixture and the catalyst at 323-523 K enabled the separation of liquid

alkylbenzenes. The authors of this article sought to study the reaction in detail. Products were isolated from solutions with the ratio  $R^1R^2CO:H_3PW_{12}O_{40} = 30:1$ , held several months at 293 K by extraction in DMSO and  $CCl_4$ . Both the carbonyl compound molecules and the products of their condensation become reactive as a result of formation of complexes with protons with the participation of a heteropolyanion. The end product of the polycondensation of acetone is not the polymethylvinylene that was produced by Kargin et al. (DOKL. AN SSSR, 1960, Vol 134, No 5, p 1098); rather the polycondensate is formed of fragments present in the primary condensation products, joined in an irregular manner. The solid product of polycondensation of acetone and the oily products of polycondensation of methylethylketone are studied to determine their structural and thermal characteristics. References 3 (Russian).

UDC 543.422.4:541.128:541.183

**IR Spectra of Catalysts and Adsorbed Molecules. Report 38. Zinc-Containing Pentasils: Acid Properties and Conversion of Ethane**

18410168d Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA No 3 Mar 89 (manuscript received 14 Dec 87) pp 524-528

[Article by L. I. Lafer, Zh. L. Dykh, V. I. Yakerson, V. P. Sitnik, T. V. Vasina, O. V. Bragin, Institute of Organic Chemistry imeni N. D. Zelinskiy, USSR Academy of Sciences, Moscow]

[Abstract] Continuing previous studies, the authors investigate the acidity of zinc-containing pentasils and their activity in the aromatization of ethane and attempt to determine the reasons for increasing activity and selectivity in modified catalysts. The zinc ions in the pentasil are included in cation-exchange sites which are strong B-centers. The zinc-HZSM systems generally have two types of B-centers (strong and weak) and three types of L-centers (lattice,  $Zn^{2+}$  in cation-exchange sites, and  $Zn^{2+}$  in the composition of an excess phase or  $ZnO$  cluster). The aromatizing activity increases when  $Zn^{2+}$  is added, reaching a maximum when there is a complete exchange of protons in cation-exchange sites for  $Zn^{2+}$ . The  $Zn^{2+}$  ions not located at cation-exchange sites cause secondary reactions of methane formation and condensation. Figures 3; References 15: 8 Russian, 7 Western.

UDC 542.97:547.213:547.212

**Catalytic Properties of Pentasil-Containing Compositions in Hydrocarbon Conversion Reactions. Report 2. Conversion of Propane and Ethane on Zn-Modified Pentasils**

18410168e Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA No 3 Mar 89 (manuscript received 30 Dec 87) pp 528-533

[Article by T. V. Vasina, V. P. Sitnik, A. V. Preobrazhenskiy, L. I. Lafer, V. I. Yakerson, O. V. Bragin, Institute of

Organic Chemistry imeni N. D. Zelinskiy, USSR Academy of Sciences, Moscow]

[Abstract] Catalytic methods and IR spectroscopy are used to study the transformation of propane and ethane on Zn-containing pentasils and to ascertain the nature of the modifying effect of Zn and its optimal concentration in an Zn/HZSM system. The most effective catalysts for aromatization of lower alkanes are pentasils containing 0.5-1% Zn; increasing the Zn content to 5% accelerates methane formation considerably. Aromatization of propane on Zn-containing pentasils is accompanied by the development of catalysts and a growth in the aromatizing activity of the system during the reaction, which is linked to the change in the state of the Zn brought about by the interaction between the zinc and carrier and by the reaction medium. IR spectroscopy demonstrates that when pentasils are modified by  $Zn^{2+}$ , the strong acidic Brönsted centers gradually disappear, and new strong Lewis centers—which facilitate the activation of lower alkanes as a result of electron-acceptor properties—are formed. Figures 3; references 12: 7 Russian, 5 Western.

UDC 541.124:542.941.7:547.546:541.49:546.97

**Study of Catalytic Activity of Metal Complexes Fixed on Solid Carrier. Report 6. Reduction of Nitrobenzene and Its Halogen Derivatives by Chemically Bonded Hydrogen in Presence of Immobilized Rh Complexes**

18410168f Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 3 Mar 89 (manuscript received 11 Nov 87) pp 534-539

[Article by V. Z. Sharf, V. F. Dovganyuk, V. I. Isayeva, and B. I. Maksimov, Institute of Organic Chemistry imeni N. D. Zelinskiy, USSR Academy of Sciences, Moscow]

[Abstract] The catalytic properties of Rh complexes immobilized on silica gels containing amino groups and aminophosphine groups in the reduction of nitrobenzene and various halogen nitrobenzenes by transfer of hydrogen from propanol-2 and  $NaBH_4$  are studied. The rhodium complexes are found to catalyze selective reduction of nitrobenzene to aniline by transfer of hydrogen from propanol-2 and sodium borohydride in argon. The reduction rate of nitrobenzene by sodium borohydride is one to two orders of magnitude greater than by propanol-2. The introduction of the halogen to the benzene ring decreases the nitro group reduction rate. Reduction of halogen nitrobenzene by sodium borohydride occurs in two stages: reduction of the  $NO_2$  group followed by the splitting out of the halogen. Figures 3; References 7: 4 Russian, 3 Western.

UDC 541.128:34:541.49:546.97

### Displacement of Water Gas in Liquid Phase: Catalysis by Water-Soluble Phosphine Complexes of Rhodium

18410168g Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 3, Mar 89 (manuscript received 4 Sep 87) pp 542-549

[Article by Ye. G. Chepaykin, A. P. Bezruchenko, Ye. N. Salnikova, F. Yo, Z. Tom, M. T. Bek, M. L. Khidekel, Institute of Structural Macrokinetics, USSR Academy of Sciences, Chernogolovka; Department of Institute of Chemical Physics, USSR Academy of Sciences, Chernogolovka; Layosh Koshuta University, Debrecen, Hungary]

[Abstract] Results are presented from a study of the catalytic properties of rhodium complexes containing diphenyl-*m*-sulfophenylphosphine sodium salt  $\text{PPh}_2\text{C}_6\text{H}_4\text{SO}_3\text{Na}$ —and later  $\text{PPh}_2\text{Ph-s}$ —as the ligand in liquid-phase water gas displacement. A reaction mechanism that has two possible paths and does not contain haloid ions is suggested for the process. The mechanisms will require more detailed kinetic study to verify them, but the key intermediates and their sequence in the reaction mechanisms diagrammed in the article reflect the essence of the process reliably and agree with the data from the literature on the mechanism of liquid-phase water gas displacement in similar systems. Figures 2; References 15: 4 Russian, 11 Western.

UDC 541.128.34:547.553.1:541.515

### Activity of Secondary Aromatic Amines As Catalysts of Sterically Hindered Aroxyl Radical Reaction with Hydroperoxide

18410168h Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 3 Mar 89 (manuscript received 16 Nov 87) pp 549-557

[Article by V. T. Varlamov, Institute of Chemical Physics, USSR Academy of Sciences, Chernogolovka]

[Abstract] A study is made of the variation in catalytic activity of AmH aromatic amines as a function of temperature and nature of substituents in the aromatic rings. The rate of the catalytic reaction is found to be proportional to  $[\text{ArO}^\cdot]$ ,  $[\text{ROOH}]$ , and  $[\text{AmH}]$  and inversely proportional to  $[\text{ArOH}]$ . The catalytic constant is found for 11 secondary aromatic amines in the reaction of 2,4,6-tri-*tert*-butylphenoxyl radical with cumyl hydroperoxide in  $\text{CCl}_4$  at 298.2-341.6 K. Several estimates are presented of N-H bond strength and other parameters in the amine molecules. Figures 4; References 17: 11 Russian, 6 Western.

UDC 541.64:542.952:546.821

### Study of Deactivation of Ziegler-Type Titanium Catalytic System

18410170F Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 31 No 3, Mar 89 (Seriya A) (manuscript received 11 Aug 87) pp 514-518

[Article by V. B. Murachev, M. V. Terganova, I. F. Kuzkina, I. G. Makarov, Ye. F. Shashkina, N. N. Byrikhina, V. M. Kazakova, and V. I. Aksenov, Moscow Institute of Precision Chemical Technology imeni M. V. Lomonosov]

[Abstract] A study is made of the change in activity of the titanium catalytic system  $\text{TiI}_2\text{Cl}_2\text{-Al(iso-C}_4\text{H}_9)_3$  during polymerization of butadiene and the variation of this activity with the Al:Ti ratio. A comparison of kinetic experimental data with data from EPR spectroscopy indicates that the rapid drop in catalytic activity in the system with an increasing Al:Ti ratio results from deeper reduction of the titanium atom. Figures 3; References 23: 15 Russian, 8 Western.

UDC 541.64:547.258.11

### Immobilization of Organotin Catalyst on Polymer Carrier To Activate It in Urethane Formation

18410170G Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 31 No 3, Mar 89 (Seriya A) (manuscript received 14 Aug 87) pp 519-525

[Article by P. A. Berlin, M. A. Levina, R. P. Tiger, and S. G. Entelis, Institute of Chemical Physics, USSR Academy of Sciences]

[Abstract] A study is made of the kinetics of urethane formation with a catalyst consisting of a copolymer of maleic anhydride with styrene. The organotin catalyst is highly active due to the limited participation of catalytic centers in inactive heterogeneous associates and the possibility of new paths for the formation of the reaction product. The transition from traditional low-molecular-mass catalysts to binuclear analogues and polymer catalysts is found to change the mechanism of the elementary act of catalysis. Molecular organization of the catalytic complex by interaction of functional groups containing catalytic centers is clearly seen. Quantitatively comparing the regularities of catalysis on polymer carriers that help to organize the polynuclear structure of a "microreactor" with the data obtained on the basis of low-molecular-mass models is a difficult task that will require the development of a special research methodology. Figures 3; References 18: 12 Russian, 6 Western.

UDC 541.128.13:541.13

**IR-Spectroscopic Study of Adsorption of CO on  
Ni-Pd/Al<sub>2</sub>O<sub>3</sub> Catalysts**

18410179b Tbilisi SOOBSHCHENIYA AKADEMII  
NAUK GRUZINSKOY SSR in Russian  
Vol 131 No 3, Sep 88 pp 533-537

[Article by N. G. Girogadze, S. V. Yushin, A. A. Vedenyapin, G. O. Chivadze]

[Abstract] With the use of CO adsorption, an IR spectroscopic study is made of the active phase state in bimetallic Ni-Pd/Al<sub>2</sub>O<sub>3</sub> catalysts with varying ratios of active metals, and the specific properties of the catalysts are investigated. The catalysts were made by soaking  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with aqueous solutions of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and H<sub>2</sub>PdCl<sub>4</sub>, with subsequent drying and oxidation in oxygen at 450°C for one hour. It is suggested that the centers of adsorption of carbon monoxide in Ni-Pd catalysts are sets of atoms containing Pd and Ni (Ni-Pd clusters), with some electron interaction between the Pd and Ni. Figures 1; references 7: 1 Russian, 6 Western.

UDC 543.544

**Operational Characteristics of Aerosil-Based Colloidal Stationary Phases**

18410151b Moscow *ZHURNAL ANALITICHESKOY KHIMII* in Russian Vol 44 No 2, Feb 89 (manuscript received 9 Dec 87) pp 230-233

[Article by S. I. Kirsh, T. N. Fomicheva, N. T. Karabanov, and M. S. Vigdergauz, Chemistry SRI at Gorky State University imeni N. I. Lobachevskiy]

[Abstract] Colloidal stationary phases based on highly dispersed silica adsorbents (aerosils) and heat resistant organic liquids have found applications in gas chromatography. Attributes of such systems include the possibility of controlling liquid-phase and adsorbent properties, high efficiency and thermal stability, ease of preparation, and universal application. Aerosil-based colloidal sorbents have thus been used to solve diverse

problems in the chromatographic determination of both organic and element-organic compounds. Experience in research and applications has shown that, in operation, colloidal stationary phases do not differ from conventional homogeneous separation systems. However, since colloidal systems are two phased, traditional concepts of the thermodynamic instability of colloidal systems made it doubtful that reproducible columns containing this type of sorbent could be prepared or that stable retention characteristics at high temperatures could be obtained. In the present work a study was made of the operational characteristics of colloidal stationary phases based on polyethylene glycol and aerosil. It was demonstrated that the reproducibility of a colloidal sorbent preparation does not differ from that of a sorbent prepared with pure polyethylene glycol and that colloidal sorbents are sufficiently stable for operational use. The maximum operating temperature of a column containing a colloidal sorbent is higher than that of one containing a pure liquid. Figures 3; references 5 (Russian).

UDC 546.214+535.211

**Features of Thermal Ignition of Ozone-Containing Mixture at Low Pressures**

18410161c Moscow VESTNIK MOSKOVSKOGO  
UNIVERSITETA: SERIYA 2, KHIMIYA in Russian  
Vol 30 No 1, Jan-Feb 89 (manuscript received  
21 Jul 87) pp 35-38

[Article by B. S. Lunin, O. V. Kuricheva, V. V. Timofeyev, and Yu. N. Zhitnev, Chair of Physical Chemistry]

[Abstract] Utilizing infrared laser radiation to initiate thermal ignition of gas mixtures presents new opportunities for a more detailed study of this process. Laser heating makes it possible to achieve homogeneous ignition of a gas mixture at sufficiently low reagent pressures

and total exclusion of the otherwise dominating influence of the heterogeneous step during the initial stage of the process because the reactor walls remain cold. This method of thermal initiation is especially suitable for studying explosive decomposition of a thermodynamically unstable compound such as ozone. The accepted practice has been to study the ignition of ozone and its mixtures at ozone partial pressures of 5 mm Hg or above. In the present work reagent pressures of 1.0-2.0 mm Hg are employed. The purpose of the work is to determine the concentration and temperature limitations of thermal decomposition of ozone in gas mixtures containing sulfur hexafluoride as an IR-sensitizer under the action of a pulsed carbon dioxide laser. The results show that the thermal explosion initiated by an IR-laser is well described by equations for the stationary theory of explosion. Figures 2; references 14 (Russian).



UDC 541.122.3;537.311.3;546.311'.47'.131

**Molar Volume and Conductivity of Chlorides of Tin, Ammonium, and Guanidonium**

18410155C Kiev UKRAINSKIY KHIMICHESKIY  
ZHURNAL in Russian Vol 55 No 2, Feb 89  
(manuscript received 23 Dec 87) pp 138-141

[Article by T. V. Lesnichaya, V. D. Prisyazhnyy, G. G. Yaremchuk, and Yu. V. Kosov, Institute of General and Inorganic Chemistry, Ukrainian Academy of Sciences, Kiev]

[Abstract] A study is made of the density and conductivity of melts in the ternary system  $\text{GuCl-NH}_4\text{-ClSnCl}_2$ , and the molar volume and conductivity are calculated. A comparison of experimental data and data calculated by two equations derived in this article is presented. The comparison indicates that one equation is suitable for computation of the molar volume of the melts in a ternary system with a common anion when all three binary components deviate from additivity. The second equation can be used to estimate the molar conductivity of ternary salt melts based on the data on their binary components. Figures 3; References 7: Russian.

UDC 546.41+532.733

**Influence of Calcium on Resistance of Films Obtained by Decomposition of Thermally Sensitive Copper Salts**

18410162B Novosibirsk IZVESTIYA SIBIRSKOGO  
OTDELENIYA AKADEMII NAUK SSSR: SERIYA  
KHIMICHESKIKH NAUK in Russian No 1, Jan 89  
(manuscript received 19 Mar 87) pp 54-58

[Article by O. V. Sander, S. G. Mamylov, O. I. Lomovskiy, Institute of Solid-state Chemistry and Processing of Mineral Raw Materials, Siberian Division, USSR Academy of Sciences, Novosibirsk]

[Abstract] A study is presented of the influence of calcium ion complex formation in a dielectric activation solution on electrical resistance of the current-conducting layer. It is found that a solution of thermally sensitive copper hypophosphite obtained in an exchange reaction of copper sulfate and calcium hypophosphite contains significant quantities of calcium, up to 15 g/l with copper (II) concentration in the solution 45 g/l. The quantity of calcium salt in the conducting coating formed on the dielectric after decomposition of the copper salt and washing can be regulated by adding trilon B to the solution. Introduction of trilon B facilitates washing of the calcium salts from solid products of thermal decomposition of the thermally sensitive copper salt and improves the structure of the metallic film obtained in the final operation of galvanic copper coating. Figures 4; References 4: Russian.

UDC 542.61:546.92:546.98

**Extraction of Halide Complexes of Pt(IV) and Pd(II) With Dipyrazolonyl-Methane and its Homologs and Analysis by Atomic Emission Spectroscopy**

18410174b Moscow ZHURNAL ANALITICHESKOY  
KHIMII in Russian Vol 44 No 3, Mar 89 (manuscript  
received 22 Dec 87) pp 455-460

[Article by M. I. Degtev, N. Ye. Vorobyeva, and Yu. A. Makhnev, Perm State University imeni A. M. Gorkiy]

[Abstract] Technical details are presented on the extraction of Pt(IV) and Pd(II) from  $\text{H}_2[\text{PtCl}_6] \cdot \text{H}_2\text{O}$  and  $\text{PdCl}_2$ , respectively, with dipyrazolonylmethane and a number of its alkyl homologs (e.g., -ethane, -propane, -butane, -pentane, -heptane, -octane). Under optimal conditions and a ratio of the aqueous to organic phase of 50:1 a single extraction procedure led to the recovery of 96% or better of the Pd and 90-92% of the Pt in the sample. Re-extraction was best achieved with 0.01 M NaOH, while HCl,  $\text{HNO}_3$ ,  $\text{NH}_3$ , and EDTA provided less than optimum conditions. Subsequent atomic emission analysis yielded results with  $s_r$  values in the 0.06 to 0.12 range. The use of dipyrazolonylethane and its congeners was also found effective in separation of Pt(IV) and Pd(II) from the following heavy metals: Ag, Fe(III), Hg, Zn, Cd, Cu(II), Ni, Pb, and Cr(III). Figures 3; references 16 (Russian).

UDC 541.135:541.183.12

**Electrotransfer of Ions Through Diffusion Layer With Disrupted Electroneutrality**

18410167A Moscow ELECTROKHIMIYA in Russian  
Vol 25 No 3, Mar 89 (manuscript received 12 Sep 84;  
after revision 26 Oct 87) pp 301-306

[Article by V. V. Nikonenko, V. I. Zabolotskiy, and N. P. Gmusin, Kuban State University, Krasnodar]

[Abstract] An approximate analytic solution is obtained for a system of equations describing the transmission of electrical current through a diffusion layer near a membrane with unipolar conductivity. The approximate solution generated can be used to find the distribution of concentrations and potential in the diffusion layer. Due to the simplicity of the solution, it can also be used to solve more complex problems of diffusion electrochemical kinetics. The distribution of concentrations in the diffusion layer is compared with its voltage-current characteristic with a fixed concentration of counterions at the interface with the membrane. Figures 3; References 5: 9 Russian, 6 Western.

UDC 541.138.3 12

**Possibility of Formation of Hydrogen Amalgam at High Negative Electrode Potentials**

18410167B Moscow ELEKTROKHIMIYA in Russian  
Vol 25 No 3 Mar 89 (manuscript received 28 Jan 85) pp 307-12

[Article by Ye. G. Tsventarnyy, T. G. Nikiforova, and Ye. A. Mishnina, Leningrad State University]

[Abstract] A study was made of the formation of a hydrogen amalgam on a mercury electrode at high negative potentials due to an increase in the activity of the atomic hydrogen formed under these conditions. The studies were performed by measuring the curves of the drop in electrode potential with time after disconnection of cathodic polarization in a galvanostatic mode. The studies were performed in alkaline solutions of ammonium chloride, tetramethyl ammonium, and hydrochloric acid at various concentrations at 25 °C. The data indicate that, at high negative potentials of the mercury electrode, atomic hydrogen obtained either by decomposition of ammonium amalgams or direct reduction of hydrogen molecules or hydroxonium ions can accumulate in the mercury and form an amalgam. Figures 5, References 8: 5 Russian, 3 Western.

UDC 541.138:620.194

**Electroextraction of Hydrogen From Metal With Superimposed Isotropic Diffusion, Formal Surface Reaction, and Reversible Trapping**

18410167C Moscow ELEKTROKHIMIYA in Russian  
Vol 25 No 3, Mar 89 (manuscript received 23 Jan 86; after revision 14 Jul 88) pp 313-320

[Article by N. G. Krapivnyy, V. I. Sobornitskiy, and V. I. Chernenko, Dnepropetrovsk Chemical Technological Institute imeni F. E. Dzerzhinskiy]

[Abstract] Based on a solution of a previously obtained diffusion problem, a study is made of the case in which the rates of diffusion and adsorption are comparable whereas the mechanism of the process of electrochemical extraction of hydrogen remains constant over time. The mechanism of hydrogen transfer is based on the assumption that the solid phase is isotropic while the hydrogen diffusion coefficient is independent of concentration. Methods are presented for computing the rate constants and estimating the contribution of the interaction of hydrogen with solid-phase structural defects to the total inhibition of the reaction. The initial uniform distribution of hydrogen through the cross section of the specimen and zero transfer of hydrogen through the phase interface opposite the electroextraction interface are assumed. Figures 7; References 14: 7 Russian, 7 Western.

UDC 541.135.4

**Properties of Nickel Produced by High-Speed Electrochemical Precipitation**

18410167D Moscow ELEKTROKHIMIYA in Russian  
Vol 25 No 3, Mar 89 (manuscript received 26 Nov 86) pp 321-325

[Article by Ye. V. Artamonova, M. L. Levit, I. V. Tsvetkov, Yu. D. Gamburg, and A. D. Davydov, Experimental Scientific Research Institute of Metal-Cutting Machine Tools, Moscow]

[Abstract] A study is made of the influence of high-speed electrolysis parameters on the properties and structure of thick nickel precipitates on a copper substrate in a sulfamine-acid electrolyte at a pH of 3.5 to 3.9 and a temperature of -50°C. It is found that, upon high-speed cathodic shape formation, nickel precipitates have greater hardness than under ordinary conditions and comparatively low internal stresses. After completion of the electroprecipitation, the precipitates undergo relaxation processes that are accompanied by a decrease in hydrogen content, hardness, and internal stresses. Figures 5; References 12: 10 Russian, 2 Western.

UDC 541.135:535.34

**Electrooptical Characteristics of Electrochromic Nickel Oxide Electrode in Potentiodynamic Mode**

18410167E Moscow ELEKTROKHIMIYA in Russian  
Vol 25 No 3, Mar 89 (manuscript received 14 Oct 87) pp 336-342

[Article by G. E. Bayars, Ya. A. Pitkevich, A. R. Lasis, E. V. Pentyush, Yu. A. Benders, and V. V. Bets, Latvian State University imeni P. Stuchka, Riga]

[Abstract] Results are presented from a study of changes in the electrooptical parameters of an electrochromic nickel-oxide electrode in a potentiodynamic mode during electrocoloration and decoloration. The results are produced by cyclical voltage-current measurement with scanning of the potential reverse point and measurement of light transmission. The thin-film nickel-oxide electrode studied was produced by magnetron atomization. It is found that only a small portion of the mass of the electrode is electrochemically active. Under potentiodynamic conditions, the parameters of the electrode are essentially determined by the current-dependent component of the emf. When changes in the charge-dependent portion of the emf are compensated by the current-dependent portion, the differential capacitance of the electrode approaches infinity. Figures 3; References 6: 4 Russian, 2 Western.

UDC 541.138

**Electrocatalytic Activity of Palladium and Its Alloys With Zirconium, Silicon, and Copper in Oxidation of Methanol, Formic Acid, and Formaldehyde***18410167G Moscow ELEKTROKHIMIYA in Russian Vol 25 No 3, Mar 89 (manuscript received 22 Jun 88) pp 369-375*

[Article by N. S. Kopylova, O. A. Petriy, Yu. V. Yefimov, L. I. Voronova, and F. M. Spiridonov, Moscow State University imeni M. V. Lomonosov]

[Abstract] The purpose of this work was to compare the electrocatalytic activity of the amorphous and crystalline alloys mentioned in the title in the oxidation of methanol, formic acid, and formaldehyde and to compare the properties of these alloys with the properties of polycrystalline palladium. The experimental results show that the amorphous and crystalline alloys Pd-Si and Pd-Si-Cu have approximately the same activity under steady conditions, less than that of palladium and Pd-Zr. The mechanism of oxidation of the organic substances studied is the same on the alloys as on palladium. The differing influence of etching of Pd-Zr alloys in HF on their activity in different processes is apparently due to the fact that these reactions occur with the formation of various intermediate chemically sorbed compounds and by different mechanisms. Amorphous and crystalline Pd-Zr alloys show electrocatalytic activity superior to that of palladium in the oxidation of methanol and formaldehyde. Figures 7; References 18: 5 Russian, 13 Western.

UDC 539.216.2:538.24

**Influence of Electrolytic Precipitation Conditions on Formation of Columnar Structure of Cobalt Film***18410167F Moscow ELEKTROKHIMIYA in Russian Vol 25 No 3, Mar 89 pp 359-363*

[Article by A. V. Boltushkin, T. A. Tochitskiy, and V. M. Fedosyuk, Institute of Solid State Physics and Semiconductors, Belorussian Academy of Sciences, Minsk]

[Abstract] A study is presented of the change in structure of cobalt films as a function of precipitation conditions (current density and pH) and film thickness. Cobalt films of 20 mm to 2  $\mu$ m thick were precipitated onto copper foil from a sulfuric acid electrolyte at 20°C, 5-100 mA/cm<sup>2</sup>, and a pH of 5 to 7.4. The film texture was determined by an electronographic method in reflection. The microstructure was studied with an electron microscope in transmission, and the surface morphology was studied by the method of replicas. Depending on the crystallization conditions, a columnar crystallite structure is produced with preferential orientation of (001) faces parallel or perpendicular to the plane of the specimen. These structural peculiarities are the main cause of

differences in magnetic properties and magnetization mechanisms and are the main reason why the materials may be used as information-carrying media in devices with both vertical and longitudinal recording methods. Figures 2; References 13: 5 Russian, 8 Western.

UDC 541.135.5

**Electrochemical Behavior of Polydimethyldiallylammonium Chloride Electrode in Sulfolane Lithium Chloride Solutions***18410167H Moscow ELEKTROKHIMIYA in Russian Vol 25 No 3, Mar 89 (manuscript received 18 Aug 87) pp 399-401*

[Article by V. S. Kolosnitsyn, A. A. Yakovleva, and Yu. Ye. Nikitin, Institute of Chemistry, Bashkir Affiliate, USSR Academy of Sciences, Ufa]

[Abstract] A study is made of the basic electrochemical behavior of anion-exchange membranes in electrolytic systems based on aprotic dipolar solvents. The studies showed that membranes of polydimethyldiallylammonium chloride in sulfolane lithium chloride solutions have high electroconductivity. As the membrane-electrolyte equilibrium is established, significant sorption of lithium chloride occurs. Upon polarization of the membranes with high currents, the bonded lithium chloride is desorbed. This behavior is apparently characteristic for electrolytic systems based on aprotic dipolar solvents. Figures 2; References 6: 2 Russian, 4 Western.

UDC 541.135.6:669.777

**Influence of Illumination on Electroprecipitation of Tellurium in Tartrate Electrolytes***18410167I Moscow ELEKTROKHIMIYA in Russian Vol 25 No 3, Mar 89 (manuscript received 14 Sep 87) pp 404-406*

[Article by T. I. Parmanov and V. M. Bigelis, Institute of Nuclear Physics, Uzbek Academy of Sciences, Ulugbek]

[Abstract] A study is made of the influence of illumination on the cathodic process in tartrate electrolytes. Studies were performed in solutions containing 0.1-0.5 M TeO<sub>2</sub> + 2 M C<sub>4</sub>H<sub>6</sub>O<sub>6</sub> + 5 M H<sub>2</sub>SO<sub>4</sub>, recorded. The cathode was a platinum plate that had been electrolytically coated with tellurium from the solutions studied. A 500-W incandescent light bulb was used. The cell was thermostatted at 25°C. An empirical equation is derived to explain the observed depolarization under the influence of light on the photopotential  $E_p$ :  $E_p$  equals 0.1 (1 +  $I_c$ ), V. This behavior of the electrode is explained by the fact that, as the thickness of the coating and current density increase for the p-type semiconductor, a significant shortage of electrons develops in the space-charge area and the concentration of electrons on the surface is greatly reduced, thus decreasing the rate of the electrochemical reaction and increasing the electrode polarization. Illumination generates additional electrons, and the

reaction rate increases, which causes a decrease in electrode polarization. Figures 4; References 5: Russian.

UDC 541.138

**Corrosion-Electrochemical Behavior of  
Press-Composition Carbon- Reinforced Plastics**

18410167J Moscow *ELEKTROKHIMIYA* in Russian  
Vol 25 No 3, Mar 89 (manuscript received  
29 Sep 87) pp 406-409

[Article by F. I. Danilov, A. B. Velichenko, S. M. Loboda, and R. L. Mokiyeenko, Dnepropetrovsk Institute of Chemical Technology imeni F. E. Dzerzhinskiy]

[Abstract] A study is made of the corrosion-electrochemical behavior of pressed composite carbon-reinforced plastic materials based on phenolformaldehyde resin with random short hydrate cellulose or polyacrylonitrile carbon fibers with 70 percent filling. Experiments were performed in 3.0 M  $(\text{NH}_4)_2\text{SO}_4$  and a chromating electrolyte. The carbon-reinforced plastics were almost 50 times more resistant to anodic polarization destruction than was low-porosity graphite, being inferior only to titanium dioxide-manganese anodes. Carbon-reinforced plastic electrodes have comparatively high resistivity, which hinders polarization measurements. The studies make it possible to recommend pressed composite carbon-reinforced plastics based on phenolformaldehyde resin reinforced with carbon fibers as anodes for various processes that are sensitive to oxidation of the components of the electrolyte. Figures 2; References 14: 11 Russian, 3 Western.

UDC 66.011

**Catalytic Purification of Exhaust Gases in Plasticizer Production***18410205D Kiev KHIMICHESKAYA**TEKHNOLOGIYA in Russian No 2, Mar-Apr 89**(manuscript received 3 Apr 87) pp 85-90*

[Article by V. A. Chumachemko, L. Yu. Zudilina, A. I. Labenskiy, T. V. Mulina, and Yu. Sh. Matros, Special Design and Technology Office of Catalysts, Novosibirsk]

[Abstract] A nonsteady catalytic method has been developed for purifying wastes from the production of plasticizers of phthalic anhydride and  $C_4$ - $C_8$  alcohols. The

method has been implemented on a pilot scale, and preliminary testing of various oxide-type catalysts has resulted in the selection of an aluminum-copper chromium catalyst, IKT-12-8. Further studies were undertaken to determine the kinetics of the deep oxidation of multicomponent mixtures of the required composition and content in the exhaust gases. The basic technological and design characteristics of the reactor are described. The reactor managed to remove 99-99.6 percent of the toxic wastes in the exhaust gases, which conforms to the requirements regarding the maximum permissible concentration of toxic substances in the workplace. The activity of the catalyst decreased by about 50 percent over 1.5 years of operation of the reactor but remained at a sufficiently high level to continue achievement of the good results. Figures 3; References 6: Russian.

UDC 631.82:631.582

**Effectiveness of Mineral Fertilizers in Intensive Fodder Crop Rotation**

18410175a Moscow AGROKHIMIYA in Russian  
No 3, Mar 89 (manuscript received 12 Feb 88) pp 75-78

[Article by P. R. Shott, Kemerovo Scientific Research Institute of Agriculture]

[Abstract] A multiyear (1983-1986) assessment was conducted on the efficacy of mineral fertilizers in intensive fodder crop (vetch, sweet clover, oats, spring rape, winter rye) rotation under the soil and climatic conditions prevalent in Western Siberia. The data demonstrated that the employment of N120P50K80 fertilizer on the leached chernozem soils of the forest-steppe zone increased productivity of the fields from a mean of 36 to a mean of 59 quintals/ha in terms of dry substance, or by 64% on the average. The increased harvests were accompanied by increased uptake of nutrient elements by the crop biomass. The increase in the case of nitrogen, phosphorus, and potassium was 93, 75, and 85%, respectively, with the nutrient balance as percentage of the loss due to utilization (excluding nitrogen fixation by legumes) coming to 83 for nitrogen, 120 for phosphorus, and 49 for potassium. References 7 (Russian).

UDC 631.862:636.086.3

**Transformation of Nitrogen, Phosphorus, and Potassium Derived From Mineral and Organic Fertilizers Used Under Fodder Crops**

18410175b Moscow AGROKHIMIYA in Russian  
No 3, Mar 89 (manuscript received 2 Feb 88) pp 79-83

[Article by T. I. Makarova, All-Union Scientific Research Institute of Fodder, Lugovaya, Moscow Oblast]

[Abstract] Trials were conducted under controlled conditions on the effects of mineral fertilizers N150P90K180 and liquid manure on nitrogen balance and fractional composition of phosphorus and potassium when used for fertilization of maize and barley on dernovo-podzolic soil. The uptake factor for nitrogen derived from manure was 2% greater for barley and 7% greater for maize than for nitrogen provided by ammonium nitrate. Penetration of nitrogen provided by ammonium nitrate to a depth of 35 cm was 20-50% greater than for nitrogen derived from manure, and to a depth of 100 cm some 16-20% greater. Additional determinations of unaccountable losses of nitrogen and its immobilization in the soil indicated that both forms of fertilizer were essentially comparable in effectiveness. Introduction of phosphorus as manure and superphosphate led to an increase in the assimilable phosphorus fraction until the midpoint of plant growth, with the fractional composition stabilizing thereafter. Both forms

of fertilizer led to an increase of assimilable potassium that was fully utilized by the crops during their growth. References 7 (Russian).

UDC 631.811:633.2

**Nutrient Levels and Quality of Timothy Grass Hay on Peat Soil in Western Regions of Belorussian Polesia**

18410175c Moscow AGROKHIMIYA in Russian  
No 3, Mar 89 (manuscript received 6 Apr 88) pp 84-91

[Article by V. D. Sudakov, A. I. Dylko, Yu. M. Tashpulatov, Z. A. Polyukh, L. N. Sudakova, V. G. Shershovets, N. P. Yanushkevich, and L. N. Kozlovich, Brest Oblast Planning and Research Station for Chemicalization of Agriculture]

[Abstract] Multifactorial studies were conducted on timothy grass grown on pH 5-5.5 peat soil in the Western regions of Belorussian Polesia, in order to determine the various factors that provide quality fodder for cattle. The data demonstrated that quality estimates cannot be based only on the content of protein, carotene, non-nitrogenous extractable substances, or other organic compounds. Important in quality assessment are also the concentrations of minerals (P, Ca, Mg, K, Na,  $\text{NO}_3^-$ ), as well as Ca:P, K:(Ca + Mg), and K:Na ratios. The ratio parameters have been shown to be very sensitive to the levels of NPK and the N:P:K component ratio. Taking into consideration climatic conditions, the judicious use of proper fertilizers may be used for the production of timothy grass hay of high nutrient value in yields at the level of 100-110 quintals/ha. References 15: 1 Belorussian, 14 Russian.

UDC 581.143:635.35

**Use of Plant Growth Regulators in Cauliflower Cultivation**

18410175d Moscow AGROKHIMIYA in Russian  
No 3, Mar 89 (manuscript received  
22 Mar 88) pp 101-104

[Article by A. D. Shishov and G. L. Matevosyan, Leningrad Agricultural Institute]

[Abstract] Field trials were conducted with MOVIR-74 cauliflower to determine the effectiveness of plant growth regulators on quality and yields, with comparison of the results with seedlings and seed planting. In one series of experiments the seeds were treated with camposan (1 mg/L), CCC (500 mg/L), quartazin (1 mg/L), EBF-5 (cytokinin-like agent, 1 mg/L), or BIF-2 (cytokinin-like agent, 0.1 mg/L) for 6 h, using one liter of a preparation per 1 kg of seeds. In another series seed treatment was combined with spraying of the plants at the stage of the 3rd true leaf (400-500 L/ha). The tabulated data for the various experimental combinations demonstrated that treatment with the growth regulators increased the harvest by 12-45%, thereby raising



profitability by 1548-2611 rubles/ha. With the exception of camposan, the growth regulators enhanced the accumulation of dry substance, sugars, protein, and ascorbic acid. Furthermore, BIF-2 and EBF-5 were effective in reducing the levels of nitrates in the plants to a significant extent. Finally, treatment with the growth regulators had no effect on the taste of the plants. References 9: 5 Russian, 4 Western.

UDC 632.954

### **Trials With 'Acetal' in Maize Cultivation on Chernozem Soils**

*18410175e Moscow AGROKHIMIYA in Russian  
No 3, Mar 89 (manuscript received  
28 Apr 88) pp 105-109*

[Article by A. M. Gulidov and A. A. Krasnykh, All-Union Scientific Research Institute of Plant Protection, Voronezh Oblast]

[Abstract] Field trials were conducted in 1984-1987 in the Voronezh Oblast with the herbicide Acetal (active component: acetochlor) used in conjunction with maize cultivation. The results demonstrated that Acetal was efficient in controlling annual weeds, had no effect on perennial weeds, and had no deleterious effects on the growth and development of maize. Furthermore, the efficacy of Acetal was not affected by soil moisture. Although equally effective whether applied before planting or after sprouting, the former approach was more cost effective (a factor to be considered in view of the high cost of Acetal). The optimal dosages for Acetal ranged from 2.75 to 3.3 kg/ha, or 5 to 6 L/ha. Under various conditions of cultivation the corn harvests on Acetal-treated fields generally ranged from 106 to 128% of the control harvest. Acetal is most intensively biodegraded within the first 2 months of application, falling to 0.04-0.2 mg/kg soil after one month. Toward the end of the vegetative phase the soil levels of acetal were in the 0.03-0.07 mg/kg range. References 5 (Russian).

UDC 546.882.5.643:541.123.2

### System $Y_2O_3-Nb_2O_5$

18410155A Kiev UKRAINSKIY KHIMICHESKIY  
ZHURNAL in Russian  
Vol 55 No 2Feb 89 (manuscript received 25 Nov 87) pp  
132-134

[Article by T. G. Babich, A. V. Zagorodnyuk, G. A. Teterin, L. V. Sadkovskaya, and A. P. Zhirnova, Institute of Physics and Chemistry, Ukrainian Academy of Sciences, Odessa]

[Abstract] This study examines the state diagram of the system  $Y_2O_3-Nb_2O_5$  produced by coprecipitation from solutions heated to lower temperatures than in solid-phase synthesis, which ensures more homogeneous and stoichiometric specimens. Thermographic and x-ray phase studies indicate that x-ray amorphous precipitation products when heated undergo multistage dehydration at 120-450°C, the intermediate hydrate compounds being polymer hydroxo complexes with rare-earth element atoms coordinated to the oxygen-niobium framework through oxo or hydroxo bridges, hydroxo groups, and water molecules. A state diagram of the system is presented that indicates the formation of two compounds, an area of a  $Y_2O_3$ -based solid solution that decreases in area with increasing temperature, and broad heterogeneous areas. The liquidus curve has three eutectic points. Figure 1; References 7: Russian.

UDC 546.815'18'22'23

### Phase Equilibria in Pb-P-S (SE) Systems

18410155B Kiev UKRAINSKIY KHIMICHESKIY  
ZHURNAL in Russian  
Vol 55 No 2Feb 89 (manuscript received 13 Oct 87) pp  
135-137

[Article by I. P. Prits, M. V. Potoriy, and Yu. V. Voroshilov, Uzhgorod University]

[Abstract] A study is made of the phase equilibria in Pb-P-S (SE) systems with a parallel study of the state diagrams of ternary system cross sections in which there are ternary phases:  $PbS-P_4S^{10}$ ,  $PbS-P_2S^4$ , and  $PbSe-P_2Se^4$  (the quotation marks indicating compounds that do not exist in the systems in question). The sections  $PbS-P_4S^{10}$ ,  $PbS-P_2S^4$ , and  $PbSe-P_2Se^4$  are quasibinary because the alloys of these sections containing a superstoichiometric quantity of phosphorus and sulfur or selenium fall into the three-phase area. The studies indicate that single crystals of ternary lead hypodiphosphates can be grown by directed crystallization from a melt after first suppressing dissociation of the compound during melting. Crystals of  $Pb_3P_2S^8$  can be obtained only by vapor-phase methods. Figures 2; References 6: 4 Russian, 2 Western.

UDC 621.3.032.36:546.16

### Luminescent Properties of Solid Solutions of $CaF_2:Mn$ (Sc or Cd)

18410155E Kiev UKRAINSKIY KHIMICHESKIY  
ZHURNAL in Russian  
Vol 55 No 2Feb 89 (manuscript received 23 Dec 87) pp  
157-159

[Article by N. P. Yefryushina, Ye. A. Zhikhareva, A. V. Shamshurin, and S. V. Voyevudskaya, Institute of Physics and Chemistry, Ukrainian Academy of Sciences, Odessa]

[Abstract] A study is made of the concentration and kinetic variation of the luminescence of the  $Mn_{2+}$  ion in solid solutions of  $CaF_2:Mn$  (Me), where Me is Sc or Cd. The intensity and duration of x-radiation and the cathode ray current density were varied. X-ray excitation was selected because it is quite sensitive to changes in concentrations of luminescence centers in recombination luminophors. The optimal concentration of Mn in  $CaF_2$  was 1-1.2 percent by mass. When  $ScF_3$  or  $CdF_2$  was introduced, the maximum intensity was observed in specimens containing 0.8-1 percent Mn by mass. The kinetics of luminescence was recombination in nature and is described well by a system with one luminescence center and several deep electron traps. Figures 2; References 6: 5 Russian, 1 Western.

UDC 548.736.5

### Crystal Structure of $Ba_2SmCu_{2.75}O_{6.20}$

18410161f Moscow VESTNIK MOSKOVSKOGO  
UNIVERSITETA: SERIYA 2, KHIMIYA in Russian  
Vol 30 No 1, Jan-Feb 89 (manuscript received  
20 May 88) pp 78-81

[Article by L. M. Kovba, L. N. Lykova, V. V. Tabachenko, Ye. V. Antipov, and R. V. Shpanchenko, Chair of Inorganic Chemistry]

[Abstract] Phase studies of  $Ba_2RCu_3O_{7-y}$ , where R = rare earth metal, showed that their structure depends on the oxygen content, although these compounds are all derived from perovskite. Owing to an ordered staggering of Ba and R in the perovskite A positions, one of the periods in the lattice is structured similarly to that of  $K_2NiF_4$ . It is normally assumed that positions having coordinates 0,0,1/2 are vacant while 1/2,0,0 are partially occupied. In the case of a comparatively slight oxygen deficiency the low-temperature phase of  $Ba_2RCu_3O_{7-y}$  has rhombic symmetry, while at 600° the low-temperature phase is transformed into the high temperature tetragonal structure with static filling of the above equivalent positions. In the present work a study is made of the crystal structure of the title compound to clarify the phase structural features of  $BaRCu_{3-x}O_{7-y}$ . Figure 1; references 15: 1 Russian, 14 Western.

UDC 541.118;541.188;546.87;546.82;546.882

**Mechanical Activation of Synthesis of Layered Compounds in the System  $\text{Bi}_2\text{O}_3\text{-TiO}_2\text{-Nb}_2\text{O}_5$** 

18410162A Novosibirsk IZVESTIYA SIBIRSKOGO  
OTDELENIYA AKADEMII NAUK SSSR: SERIYA  
KHIMICHESKIKH NAUK in Russian No 1  
Jan 89 (Manuscript received 6 Sep 87) pp 28-32

[Article by Ye. G. Avvakumov, A. I. Rykov, L. M. Savchenko, V. G. Osipyan, Institute of Solid-state Chemistry and Transformation of Mineral Raw Materials, Siberian Division, USSR Academy of Sciences, Novosibirsk]

[Abstract] The method of mechanical activation is used to synthesize layered compounds and determine the reasons for accelerated synthesis as a result of activation. The high level of activation of the initial oxides does not significantly accelerate subsequent solid-phase reaction, while the formation of molecular-dense aggregates and mixing of components in the mechanical activation stage are important. The results of the studies indicate that during mechanical activation, oxides are mixed at the atomic level, resulting in the formation of a solid solution with a structure close to that of the high-temperature delta phase, and ions are redistributed to a form characteristic of the compound to be produced. Subsequent heating causes crystallization of a product with alternate layers of perovskite structure and the high-temperature delta oxide. Figures 3; References 10: 7 Russian, 3 Western

UDC 535.323

**Optical Properties of Double Molybdates and Tungstenates of Rare Earth and Alkali Metals with Sheelite Structure**

18410162C Novosibirsk IZVESTIYA SIBIRSKOGO OTDELENIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKIKH NAUK in Russian No 1 Jan 89 (manuscript received 29 Jan 88) pp 58-63

[Article by V. I. Protasova, B. M. Ayupov, L. Yu. Kharchenko, L. P. Kozeyeva, V. F. Nesterenko, Institute

of Inorganic Chemistry, Siberian Division, USSR Academy of Sciences, Novosibirsk]

[Abstract] A study is made of the optical properties of single crystals of some compounds with sheelite structure. The optical properties were studied by means of emission spectra in the 200-3000 nm band. The indices of refraction were computed and compared. The crystals of  $\text{Na}_3\text{Nd}(\text{WO}_4)_4$  were found to have the greatest forbidden zone with and the minimum index of refraction. Introduction of bismuth up to 0.5 at.% increases the index of refraction. Figures 3; References 9; 8 Russian, 1 Western.

UDC 541.49

**Synthesis and Properties of Polythiamacrocyclic Complexes of Copper***18410164b Leningrad ZHURNAL OBSHCHEY  
KHIMII in Russian Vol 59 No 2, Feb 89 (manuscript  
received 21 Jul 87) pp 359-364*

[Article by K. B. Yatsimirskiy, V. V. Pavlishchuk, and P. Ye. Strizhak, Physical Chemistry Institute imeni L. V. Pisarzhevskiy, Kiev]

[Abstract] Metal complexes with polythiamacrocyclic ligands have not been well studied, although they are of great interest to the chemistry of macrocyclic compounds of copper, silver, palladium, and other "mild" acid-cations. It has been demonstrated that copper complexes of tetrathiamacrocyclic ligands may be viewed as structural models of the so-called blue proteins that have a copper atom surrounded by a thioester group for an active site. In the present work four polythiamacrocyclic complexes of copper (II) having the composition  $\text{CuL}(\text{ClO}_4)_2$  were synthesized. The complexes turned out to be both structural and functional models of the so-called blue proteins. Figures 2; references 14: 4 Russian, 10 Western.

UDC 541.126.4

**Gas Phase Autooxidation of Tetramethyl Tin. Preparation of Stannic Oxide Films***18410164d Leningrad ZHURNAL OBSHCHEY  
KHIMII in Russian Vol 59 No 2, Feb 89 (manuscript  
received 22 Jun 87) pp 364-368*

[Article by Yu. A. Aleksandrov, Yu. Yu. Baryshnikov, I. L. Zakharov, and A. I. Charov, Chemistry Institute SRI, Gorky State University imeni N. I. Lobachevskiy]

[Abstract] Gas-phase autooxidation of alkyl compounds of tin have both theoretical and applied interest. In the present work a study was made of the oxidation of tin with tripletted oxygen under static conditions to determine stable conditions for preparing stannic oxide films. Experiments were conducted in Pyrex or quartz glass ampules. Both stationary and nonstationary conditions under which stannic oxide films could readily be prepared were determined. Gas-phase reaction products did not upset the stability of the process. Figures 2; references 6 (Russian).

UDC 547.253+547.8

**Reaction of Lithium Organic Compounds With 1,3-Dioxo-2-Silacyclohexanes and Methylchlorosilanes***18410164e Leningrad ZHURNAL OBSHCHEY  
KHIMII in Russian Vol 59 No 2, Feb 89 (manuscript  
received 30 Jun 87) pp 400-405*

[Article by V. V. Zorin, S. V. Nikolayeva, V. I. Larionov, D. M. Kukovitskiy, R. S. Musavirov, and D. L. Rakhmankulov, Ufa Petroleum Institute]

[Abstract] It has previously been demonstrated that lithium organic compounds react with alkyl- and aryl-chlorosilanes to form products of nucleophilic substitution of the chlorine atom. In the present work it was demonstrated that lithium organic compounds react with 2-chloro-1,3-dioxo-2-silacyclohexanes. The reaction passes through a stage where an electron is transferred from the lithium organic compound to the chlorosilane. This results in the formation and rearrangement of 1,3-dioxo-2-silacyclohexyl radicals and in the formation of secondary conversion products. The composition and yield of the reaction products vary with the molar ratio of the initial reagents. References 3: 1 Russian, 2 Western.

UDC 621.039:546.26:541.144.8:547.518

**Magnetic Spin Effects in Recombination and Disproportionation Reactions of Radicals in Micelle. Experimental Results***18410165d Moscow KHIMICHESKAYA FIZIKA in  
Russian  
Vol 8 No 3, Mar 89 (manuscript received 14 Mar 88) pp 347-355*

[Article by V. F. Tarasov, I. A. Shkrob, Ye. N. Step, and A. L. Buchachenko, Institute of Chemical Physics imeni N. N. Semenov, USSR Academy of Sciences, Moscow]

[Abstract] The probabilities of the recombination and disproportionation of benzoyl and sec-phenethyl radical pairs as a function of the field intensity of the external magnetic field were determined by a method based on the racemization of S(+)- $\alpha$ -methyldeoxybenzoin during its photolysis in sodium dodecylsulfate micelle. In this paper only experimental data were reported. The theoretical aspects were to be covered in a following paper. Experimentally, a change in magnetic effect sign was demonstrated in a weak (-20 E) magnetic field. The magnetic effect that was determined from the yield of other reaction products was similar to the magnetic field measured by the probability of heminal recombination. A direct proportional relationship between the recombination and disproportionation of heminal pairs induced by a magnetic field was observed across the entire range of determinations. This indicates that the reaction channels separate after the termination of spin dynamics in the radical pair. The absolute values of recombination and disproportionation in a strong magnetic field indicate either that the relaxation processes play a significant role in intercombinational conversion in the radical pair or, possibly, that the radical pair is generated in a mixed state. The probability of the recombination of benzoyl and sec-phenethyl radical pairs is 4.7-fold greater than the probability of disproportionation. Figures 4; references 22: 6 Russian, 16 Western (2 by Russian authors).

UDC 547.241

**Halogen-Substituted Methyl Phosphines and Their Derivatives**

18410161a Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: SERIYA 2, KHIMIYA in Russian Vol 30 No 1, Jan-Feb 89 pp 3-23 (manuscript received 20 Jun 87) pp 3-23

[Article by A. A. Prishchenko, A. V. Gromov, and I. F. Lutsenko, Chair of Organic Chemistry]

[Abstract] Halogen methyl organophosphorus compounds have the combined properties of both halogen and organophosphorus groups and thus attract great interest as being potentially biologically active. These compounds also provide a convenient means for studying the mutual effects of the phosphorus and halogen atoms. The present work was devoted to the synthesis and a detailed study of the properties of methyl phosphines and their derivatives containing chlorine and bromine atoms. Synthesis was based on the alkylation of phosphorus trihalide with a corresponding alkyl halide and subsequent reduction of the resulting methyl dichlorophosphite. The method was used to prepare new types of organophosphorus compounds including heterocyclics, imidophosphoric compounds, and derivatives of double-coordinated phosphorus. References 40: 27 Russian, 13 Western.

UDC 547.26'118

**Reactions of Isocyanates of Triple-Coordinated Phosphorus Acids With Hexafluoroacetone and Esters of Trifluoropyrotartaric Acid**

18410164a Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 59 No 2, Feb 89 (manuscript received 10 Jun 87) pp 278-282

[Article by I. V. Kovobalova, L. A. Burnayeva, E. K. Khusnutdinova, R. N. Kamaletdinova, and A. N. Pudovik, Kazan State University imeni V. I. Ulyanov-Lenin]

[Abstract] The unique behavior of bis-(1,1,3-trihydroperfluoropropyl)isocyanatophosphite in reactions with carbonyl compounds has been observed previously. For example, reactions with benzyl or benzoylformates result in the formation of stable 1,3,2-oxazophospholenes that are not subject to imide-amide rearrangement in contrast to unsaturated dialkylisocyanatophosphites. In the present work it was demonstrated that bis-(1,1,3-trihydroperfluoropropyl)isocyanatophosphate reacts with hexafluoroacetate in anhydrous ether at -25 to -30°C in an inert atmosphere and a 1:1 reagent ratio to form a crystalline 1:2 addition product. References 7: 6 Russian, 1 Western.

UDC 547.241

**Reactions of Diphenylchlorophosphite With Aldehydes**

18410164b Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 59 No 2, Feb 89 (manuscript received 25 Mar 87) pp 344-347

[Article by S. Kh. Nurtudinov, R. B. Sultanova, G. G. Mukhametova, T. V. Zyкова, and F. Sh. Shagvaleev, Chemical Technology Institute imeni S. M. Kirov, Kazan]

[Abstract] It has previously been demonstrated that both primary and secondary chlorophosphines react with aliphatic aldehydes at room temperature to form 1:2 addition products. In the present work it was further demonstrated that diphenylchlorophosphite also reacts with both aliphatic and aromatic aldehydes to form 1:2 addition products. In the case of diphenyl 1-(1-butenyloxy)butylphosphonate, cis-trans isomerization takes place. Figure 1; references 9: 6 Russian, 3 Western.

UDC 542.91:547.1'118

**Synthesis of Phosphine Hydrides by Reducing Isothiocyanates and Cyanides of P(III)**

18410168k Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 3, Mar 89 (manuscript received 26 Apr 88) pp 703-704

[Article by G. V. Romanov, T. Ya. Ryzhikova, E. P. Semkina, A. N. Pudovik, Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Affiliate, USSR Academy of Sciences]

[Abstract] Continuing studies of the properties of the isothiocyanates and cyanides of acids of trivalent phosphorus, the authors studied their interaction with  $\text{LiAlH}_4$ . It was found that in ether at 20°, such reactions occur with the formation of the corresponding P(III)-H derivatives, with a yield of up to 70%. The isothiocyanates and cyanides are reduced by lithium aluminumhydride to the corresponding phosphine hydrides. The phosphine hydrides that are produced are characterized by the NMR spectral data of  $^{31}\text{P}$ . References 5: 4 Russian, 1 Western.

UDC 542.91:547.1'118

**Dibutylcyanophosphite and Its Properties**

18410168l Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 3, Mar 89 (manuscript received 26 Apr 88) pp 705-706

[Article by G. V. Romanov, E. P. Semkina, A. N. Pudovik, Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Affiliate, USSR Academy of Sciences]

[Abstract] The interaction of chloranhydrides of P(III) acids with trimethylsilylcyanide usually occurs in the presence of  $\text{TiCl}_4$  and leads to the corresponding P(III) cyanides. The authors found that dibutylcyanophosphite is formed from dibutylchlorphosphite and trimethylsilylcyanide, with satisfactory yield both with and without  $\text{TiCl}_4$ . Reaction of dibutylcyanophosphite with tributylstannane in THF yields dibutoxyphosphine, a new version of the synthesis of organic phosphine hydrides. References 8 (Russian).

UDC 541.14:541.128:541.11:542.91:547.556.7:547.1'118

**Photochemical, Thermic and Thermocatalytic Interaction of Diphenyldiazomethane with Dimethylthiophosphite**

18410168m Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 3, Mar 89 (manuscript received 20 May 88) pp 726-727

[Article by B. A. Arbuzov, A. M. Polozov, N. A. Polezhayeva, A. Kh. Mustafin, Ya. A. Levin, E. I.

Goldfarb, Institute of Chemistry imeni A. M. Butlerov; Kazan State University imeni V. I. Ulyanov-Lenin]

[Abstract] Direct photolysis of a mixture of diphenyldiazomethane with dimethylthiophosphite would be expected to form a product of P-H-insertion by the mechanism of hydrogen splitting and radical pair recombination. In fact, after photolysis of this mixture, O,O-dimethyl(diphenylmethyl)thiophosphonate was identified, and the chemical nuclear polarization spectra contained a peak relating to this product. Tetraphenylethane and N-dimethoxythiophosphorylhydrazone benzophenone were also identified. The heterogeneous catalyst  $\text{CuSO}_4$  allowed carbenoid P-H-insertion into dimethylphosphite, whereas passivation occurred with dimethylthiophosphite. Carbenoid insertion into the P-H bond of dimethylthiophosphite was performed for the first time with homogeneous copper acetylacetonate. References 8: 5 Russian, 3 Western.



UDC 661.183.6.004.14

### New High-Silica Zeolites in TsVN Series

18410172a Moscow *KHIMIYA I TEKHOLOGIYA*  
*TOPLIV I MASEL in Russian No 3, Mar 89 pp 3-5*

[Article by I. Ye. Gorbatkina, L. D. Konovalchikov, B. K. Nefedov, B. L. Khusid, All-Union Scientific Research Institute of Oil Refining]

[Abstract] The authors have developed a method of synthesizing TsVN zeolites with a pentasil structure, containing 0.05-0.2% by mass  $\text{Na}_2\text{O}$ , with hydrophobic properties and an *n*-heptane adsorption capacity of 0.19-0.22  $\text{cm}^3/\text{g}$ . This article presents a study of the catalytic properties of TsVN zeolite without preliminary cation exchange in the composition of catalysts for selective hydrocracking of *n*-paraffin hydrocarbons, disproportionation of ethyl benzene and conversion of methanol. The catalysts with  $\text{Na}_2\text{O}$  of 0.06-0.19% by mass were found to be superior to catalysts based on decationated domestic TsVK and TsVM pentasils. References: 12 (Russian).

UDC 665.753.4.038

### Multifunctional Additive for Diesel Fuel

18410172b Moscow *KHIMIYA I TEKHOLOGIYA*  
*TOPLIV I MASEL in Russian No 3, Mar 89 p 6*

[Article by A. A. Gureyev, T. V. Palichev, D. M. Minkov, Moscow Institute of Petrochemical and Gas Industry imeni I. M. Gubkin]

[Abstract] With an eye to studying certain nitrogen- and oxygen-containing compounds capable of simultaneously improving chemical stability and raising cetane rating, the authors synthesized the additive ADT-1, which is based on normal paraffin hydrocarbons. Catalytic reactions were used to introduce more than 11% oxygen and more than 10% nitrogen into the additive's composition. The nitrogen that is introduced is in the form of primary amino groups. The antisludge efficiency of the additive and its stability were determined by standard methods. The additive stabilizes catalytic cracking light gas oil and improves the heat-resistance of fuel. It raises the cetane rating roughly as effectively as isopropyl nitrate, but not as effectively as cyclohexyl nitrate. The authors feel that the search for a multifunctional fuel additive should continue. References: 5 (Russian).

UDC 665.7.038

### Polyfunctional Phosphinate-Type Additives Based on Propylene Oligomers

18410172c Moscow *KHIMIYA I TEKHOLOGIYA*  
*TOPLIV I MASEL in Russian No 3, Mar 89 pp 6-8*

[Article by A. M. Levshina, D. Sh. Gamidova, M. A. Agayeva, M. Ya. Agakishiyeva, Institute of Additive Chemistry, Azerb Academy of Sciences]

[Abstract] Metal-containing phosphinate-type additives were synthesized on the basis of propylene oligomers produced at the experimental plant of the All-Union Scientific Research Olefin Institute. The molecular mass of the oligomers was 450-500; the viscosity at 100°C, 7.2-8  $\text{mm}^2/\text{s}$ ; the bromine number, 42-44  $\text{g Br}_2/100 \text{ g}$ ; and the flash point, 190-192°C. The magnesium- and calcium-containing polymer additives synthesized improve the detergent, anticorrosion and antisludge properties of motor oil. They are equal in these properties to the phosphinate IKhP-388 additive based on a copolymer of isobutylene with styrene and are recommended for use in both gasoline and diesel engines. Figure 1; references 5: 2 Russian, 1 Czech, 1 Polish, 1 Hungarian.

UDC 621.892:665.76

### Alkyl(aryl)thio(oxy)acetylhexylsulfides as Additives for Lubricating Oils

18410172d Moscow *KHIMIYA I TEKHOLOGIYA*  
*TOPLIV I MASEL in Russian No 3, Mar 89 pp 8-9*

[Article by A. B. Kuliyeu, A. G. Mamedov, M. M. Kurbanov, Institute of Additive Chemistry, Azerb Academy of Sciences]

[Abstract] Alkyl(aryl)thio(oxy)acetylhexyl sulfides were synthesized by reacting chloracetylhexylsulfides with various thiols or phenols, as well as sodium sulfide, in order to study the effect of the structure of organosulfur compounds on their efficiency as additives. The structures of the compounds synthesized were confirmed by IR and PMR spectroscopy; the purity of the compounds, by gas-liquid chromatography. Acetylhexylsulfide was studied as a prototype to determine the influence of various functional groups on the effectiveness of substituted acetylhexylsulfides. The introduction of various substituents was found to improve anticorrosion properties, the structure of the radicals affecting the properties substantially. The best overall results were obtained with benzylthioacetylhexylsulfide. References: 3 (Russian).

UDC 665.644.2

### Catalytic Cracking in the Presence of an Activating Additive

18410172e Moscow *KHIMIYA I TEKHOLOGIYA*  
*TOPLIV I MASEL in Russian No 3, Mar 89 pp 10-11*

[Article by Md. Yunus Miakh, E. M. Seid Rzayeva, M. I. Rustamov, Institute of Petroleum Processing imeni Yu. G. Mamedaliyeva, Azerb Academy of Science]

[Abstract] A study is made of the effect of an activating additive—a heavy gas oil produced at the Novobakinskiy Oil Refinery imeni Vladimir Ilich—on the process of catalytic cracking of vacuum distillate produced from Baku petroleums. The experiments were performed on a large laboratory unit with a fluidized bed

of a zeolite-containing catalyst. The results show that as the additive content increases, the output of cracking gases is almost unchanged, and the coke yield decreases, then increases. The minimum coke content on the catalyst (1.6% by mass) is achieved with the optimal additive content—2% by mass. The use of an activating additive with high aromatic hydrocarbon content decreases the formation of coke and increases the yield of the end products, whose quality is improved. Figures 1; references 6 (Russian).

UDC 665.765-404.9:621.892.261

### Effect of Excess 12-Oxystearic Acid and Calcium Hydroxide on Properties of Anhydrous Calcium Lubricants

18410172f Moscow *KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 3, Mar 89 pp 17-20*

[Article by Yu. L. Ishchuk, M. Ye. Krasnokutskaya, L. N. Dugina, R. D. Novoded, "MASMA" Scientific Production Association]

[Abstract] The literature contains virtually no information on the effect that free acids and alkalis have on the properties of anhydrous calcium lubricants based on 12-HoSt. This article studies the effect of the concentration of the additives 12-HoSt and  $\text{Ca}(\text{OH})_2$  on the properties of such lubricants and on the polymorphous conversion of  $\text{Ca}(\text{oSt})_2$  in petroleum to determine the optimal temperature of structure formation in the manufacture of the lubricants. It is found that the phase transition temperatures of  $\text{Ca}(\text{oSt})_2$  in petroleum decreases with increasing content of free 12-HoSt. Lubricants with 12-HoSt must be heat-treated based on the drop in the phase transition temperatures in the presence of 12-HoSt. The optimal heat-treatment temperature is 6-8°C below the phase transition temperature of the soap to the liquid-crystal state. Figures 2; References 18: 17 Russian, 1 Western.

UDC 621.892.092

### Synthetic Oils For Use With R22 and R502 Cooling Agents

18410172g Moscow *KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 3, Mar 89 pp 25-28*

[Article by O. N. Tsvetkov, M. A. Chagina, T. S. Dremlyukh, L. B. Silina, Ye. P. Balykina, V. P. Eyzenbeys, All-Union Scientific Research Institute of Oil Refining, Odessa Technological Institute of the Refrigeration Industry]

[Abstract] In an attempt to find lubricants satisfactory for use in refrigeration units—particularly in low-temperature piston-driven units that operate on R22 and R502 cooling agents, in which the lubricant must be soluble to temperatures of as low as -60°C—a study was made of over 100 experimental specimens of synthetic fluids, including poly- $\alpha$ -olefins, alkylbenzenes, alkyl-naphthalene, complex esters, and polyesters. The results of the study of various of the synthetic fluids confirms the promise of using ester-based lubricating compositions in refrigeration machinery. The use of synthetic hydrocarbon oils at low temperatures is limited by their poor solubility in R502. Figures 3; references 9: 6 Russian, 3 Western.

UDC 621.892:543.872:543.42

### Effect of Metals on Oxidation Stability of KS-19 Oil

18410172h Moscow *KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 3, Mar 89 pp 30-31*

[Article by A. V. Ivanov, G. M. Balak, T. S. Aleshina, N. A. Ponomarenko]

[Abstract] Some results are presented from thin-layer oxidation of KS-19 oil at high temperatures and pressures in a special installation whose working chamber consisted of a heating plate with a dome to maintain high air-pressure. Shallow metal cups made of low-carbon steel, stainless steel, copper, and aluminum were positioned on the plate and hold the oil being tested. The catalytic activity of the metals in the oxidation of the oil was estimated from the quantity of carbonyl-containing and oil-soluble metal-containing compounds detected. The rate of oxidation of the oil grows with increasing temperature and pressure, in conformance with the catalytic activity of the metals (or alloys). The ranking of catalytic activity for the metals changes with temperature. At 493 K, the catalytic activity of copper, for example, is lower than that of the low-carbon steel. At 473 K, the positions are switched. The authors explain that the catalytic activity of low-carbon steel may be due to the formation of oil-soluble compounds of iron when the oil oxidation products interact with the surface of the steel and to the action of continued oxidation. The concentration of the oil-soluble iron compounds is much lower in the oxidation on stainless steel and is independent of the oxidation conditions. At atmospheric pressure, the catalytic action of the metals on the oxidation process of the oil is negligible; whereas oxidation under pressure makes it possible to differentiate the metals in terms of catalytic activity. Figures 3; References 15: 7 Russian, 8 Western.

UDC 678.674.7'450'283.3:66.095.265

**Urethane Modification of Epoxyacrylic Compounds**

18510155F Kiev UKRAINSKIY KHIMICHESKIY  
ZHURNAL in Russian  
Vol 55 No 2Feb 89 (manuscript received 13 Oct 87) pp  
210-12

[Article by V. G. Neroznik, L. A. Podolskaya, B. G. Zadontsev, Yu. S. Zaytsev, V. I. Arshinnikova, and A. S. Burmenko, Ukrainian Scientific Research Institute of Plastics]

[Abstract] Urethane modification was performed by reacting epoxyacrylic compounds with macrodiisocyanate in order to study the influence of the modification of epoxyacrylates on the photopolymerization activity, the physicomechanical properties, and the water resistance of polymer materials based upon them. The polymer specimens used for mechanical testing were films 100-150  $\mu$  thick made on a glass substrate and irradiated with the full spectrum of a mercury-quartz lamp at 0.7 W/cm<sup>2</sup>. The results indicate the expediency of urethane modification of epoxyacrylic compounds to increase their photopolymerization activity, elasticity, and water resistance. Figures 2; References 3: 1 Russian, 2 Western.

UDC 541.64:539.199

**Torsional Skeletal Oscillations and -Relaxation in Vitreous Polymers**

18410170A Moscow VYSOKOMOLEKULYARNYYE  
SOYEDINENIYA in Russian  
Vol 31 No 3Mar 89 (Seriya A) (manuscript received 21 Jul 87)  
pp 458-463

[Article by V. A. Ryzhov and V. A. Bershteyn, Institute of Physics and Technology imeni A. F. Ioffe, USSR Academy of Sciences]

[Abstract] The  $\beta$ -relaxation of flexible-chain polymers was studied by estimating the potential barriers and scale of a unit of motion upon torsional skeletal oscillation by means of long-wave IR spectra. The figures obtained are compared with  $\beta$ -transition characteristics by using the authors' own data and data from the literature. The results indicate the correctness of the idea that the mechanism of the  $\beta$  transition is common for flexible-chain polymers. The  $\beta$  transition is a single-barrier T-G transition with torsional vibration displacement of the fragment of the chain close to the axis of rotation. Figures 2; References 28: 18 Russian, 10 Western.

UDC 541.64:539.2:5K7.458.81

**Structure and Permeability of Composite Carboxyl Membranes Based on Hydrate Cellulose**

18410170B Moscow VYSOKOMOLEKULYARNYYE  
SOYEDINENIYA in Russian  
Vol 31 No 3Mar 89 (Seriya A) (manuscript received 5 Aug 87)  
pp 469-473

[Article by G. A. Tishchenko, L. K. Shatayeva, M. Blega, I. Vatsik, K. P. Papukova, G. V. Samsonov, and Ya. Kalal, Institute of High-Molecular-Mass Compounds, USSR Academy of Sciences; Institute of Macromolecular Chemistry, Czech Academy of Sciences, Prague]

[Abstract] An experimental study is presented of the permeability of heterogeneous membranes containing fixed carboxyl groups with respect to hydrogen ions with various initial degrees of ionization of the groups. The study was performed on rigid porous membranes with virtually zero volumetric effects but with a change in the degree of ionization of the carboxyl groups. Gas adsorption and mercury porometry were used to study porosity with a fixed difference in pH on the two sides of the membrane. An estimate is presented of the kinetic constants of the interaction of the hydrogen ion with the polymer matrix. Figures 3; References 11: 4 Russian, 7 Western.

UDC 541.64:539.3

**Mechanical Properties of Vitreous Polysulfone**

18410170C Moscow VYSOKOMOLEKULYARNYYE  
SOYEDINENIYA in Russian  
Vol 31 No 3Mar 89 (Seriya A) (manuscript received 6 Aug 87)  
pp 482-485

[Article by V. N. Belousov and A. K. Mikitayev, Institute of High-Molecular-Mass Compounds, Kabardino-Balkaraskiy State University]

[Abstract] Results are presented from a study of the temperature variation of a number of the mechanical properties of polysulfone. Experiments were performed on films dried in a vacuum container at 350 K to a constant mass. The specimens were fully amorphous. Stress-strain diagrams were measured in uniaxial extension at  $8 \times 10^{-4}$  s<sup>-1</sup> in the 300-440 K temperature range. The temperature dependencies of the elasticity modulus, stress relaxation rate, failure stress, and breaking strain were found to have a bend at about 398 K, which is thus considered the quasibrittleness temperature. Figures 3; References 17: 15 Russian, 2 Western.

UDC 541.64:542.952:546.14

**Polymerization in 4-Vinyl Pyridine-Molecular Bromine System**

18410170D Moscow VYSOKOMOLEKULYARNYYE  
SOYEDINENIYA in Russian Vol 31 No 3  
Mar 89 (Seriya A) (manuscript received 7 Aug 87) pp  
497-501

[Article by Ya. Yu. Kuzyakov, V. G. Sergeyev, G. M. Lukovkin, B. Yu. Baranovskiy, and V. A. Kabanov, Moscow State University imeni M. V. Lomonosov]

[Abstract] A study is presented of the structure of a brominated poly-4-vinyl pyridine oligomer with an ionene structure that is obtained by reacting 4-vinyl pyridine with cold molecular bromine in carbon tetrachloride. The mechanism of the reaction that forms the oligomer is also studied. It is demonstrated that chlorine and iodine can also cause the polymerization observed. The two-stage reaction includes bromination of the double bond of the vinyl group with subsequent chain propagation of the reaction. Figures 4; References 6: 4 Russian, 2 Western.

UDC 541.64:542.952:546.821:547.538.141

**Low-Temperature Solid-Phase Polymerization in Styrene-Titanium Tetrachloride System**

18410170E Moscow VYSOKOMOLEKULYARNYYE  
SOYEDINENIYA in Russian Vol 31 No 3  
Mar 89 (Seriya A) (manuscript received 7 Aug 87) pp  
502-507

[Article by V. G. Sergeyev, V. Yu. Baranovskiy, G. M. Lukovkin, and V. A. Kabanov, Moscow State University imeni M. V. Lomonosov]

[Abstract] For the first time, a study is made of the low-temperature solid-phase polymerization of styrene and the influence of local mechanical action on the initiation of the process. A composition range at a molar ratio of monomer to initiator of 20:1 was found at which polymerization occurs only at the glass-crystal phase transition point in the monomer. Low-temperature polymerization forms polystyrene with broad unimodal molecular-mass distribution, regardless of the monomer-initiator ratio and local mechanical impact at 80 K. The local mechanical impact is found to form crystallization seeds at 80 K. The experimental results and data from the literature indicate that low-temperature solid-phase polymerization in metastable vitreous systems occurs in a eutectic phase that is formed from the monomer and monomer-initiator complex. Figures 5; References 19: 18 Russian, 1 Western.

UDC 541(64+49):542.954

**Synthesis and Study of Three-Dimensional Polymers Based on Trifunctional Complexes of Metals and Compounds of Silicon-Containing Vinyl Groups**

18410170H Moscow VYSOKOMOLEKULYARNYYE  
SOYEDINENIYA in Russian  
Vol 31 No 3 Mar 89 (Seriya A) (manuscript received 26 Aug 87)  
pp 573-76

[Article by N. P. Shapkin, G. M. Svystunov, and V. Ya. Shapkina, Far-Eastern Higher Engineering Marine School imeni Admiral G. I. Muvelskiy; Far-Eastern State University]

[Abstract] Cross-linked polyorganosiloxanes were obtained by 1,2-attachment of sulfenyl chloride derivatives of the acetyl acetates of chromium, aluminum, and cobalt (III) to polysiloxane (method A) and to vinyltrichlorosilane with subsequent hydrolysis (method B). Elemental analysis and IR spectroscopy are used to determine the composition and formula of the elementary links of the three-dimensional polymers produced. The aluminum-containing polymer has ion-exchange properties after acid hydrolysis. Figure 1; References 10: 7 Russian, 3 Western.

UDC 541.64:539.3

**Deformation-Strength Properties of Copolymers of Formaldehyde With 1,3-Dioxolane**

18410170I Moscow VYSOKOMOLEKULYARNYYE  
SOYEDINENIYA in Russian  
Vol 31 No 3 Mar 89 (Seriya A) (manuscript received 27 Aug 87)  
pp 577-581

[Article by O. A. Bassel, I. V. Ivankina, M. A. Kutsenko, I. G. Kuznetsova, N. F. Kedrina, and S. A. Volfson, Institute of Chemical Physics, USSR Academy of Sciences; Plastmassy Scientific-Production Association]

[Abstract] A study is made of the deformation-strength properties of copolymers of formaldehyde with 1,3-dioxolane containing 6-7 molecular percent 1,3-dioxolane. The properties are compared with those of a copolymer with a low 1,3-dioxolane content (1.2 molecular percent). The deformation properties are found to depend primarily on the molecular mass. Increasing the molecular mass causes an expansion of the range of forced elastic deformation and shifts it into the low-temperature region in copolymers with an imperfect crystalline structure. Figures 2; References 8: 5 Russian, 3 Western.

UDC 541(64+49):546.15

**Polymer Complexes of Arylacetylenes With Iodine**

18410170J Moscow VYSOKOMOLEKULYARNYYE  
SOYEDINENIYA in Russian Vol 31 No 3  
Mar 89 (Seriya A) (Manuscript received 1 Sep 87) pp  
593-596

[Article by S. G. Grigoryan, K. G. Avetisyan, G. V. Martirosyan, A. M. Arzumanyan, and A. A. Matnishyan, Armenian Affiliate, All-Union Scientific Research Institute of Reagents and Highly Pure Chemical Substances]

[Abstract] A study is presented of the polymerization of arylacetylenes in the presence of water. It is shown that the exothermic reaction of phenylacetylene and *p*-diethynylbenzene with iodine at 100-130°C, which leads to the formation of polymer complexes, involves dehalopolycondensation of the products of attachment of iodine to arylacetylene, which formed in the initial stages of the process. The mechanism is confirmed by the formation of polymers with an identical structure by the application of heat at 100-120 °C to di- and tetraiodo derivatives. Figures 4; References 5: 3 Russian, 2 Western.

UDC 678.686:537.311/312:621.3

**Influence of Thermal Shock on Service Life of Epoxy Electric Insulation Compounds**

18410177a Moscow PLASTICHESKIYE MASSY in  
Russian No 3 Mar 89 pp 28-30

[Article by S. N. Kolesov]

[Abstract] Hardened epoxy resins have good electrical-insulation and adhesive properties, plus a number of other useful qualities, such as low shrinkage, high mechanical strength, and good resistance to certain fluids. However, modulus of toughness, elongation at rupture, and glass transition temperature are poor. Thermal shock and vibration, as experienced by the electrical equipment in rolling stock, accelerate the cracking and failure of insulation. The elasticity of epoxy resin-based insulation—and thus the resistance of the insulation to thermal shock and vibration—can be improved by lowering the glass transition temperature and increasing the modulus of toughness and elongation at rupture through chemical or structural modification. The chemical modification consists of lengthening the molecular chain of the resin or hardener and introducing special compounds which interact with the resin or hardener molecules. Structural modification is performed by introducing low-molecular substances whose molecules penetrate between the macromolecules, increasing the mobility of the structural elements and improving the elasticity and flexibility of the insulation. Synthetic rubber may be used to improve the flexibility of epoxy resin. The elasticity features of several compounds are listed for various temperature ranges. References 25: 13 Russian, 12 Western.

UDC 678.675'126:539.3:543

**Influence of Moisture Content on Mechanical Properties of Polyamides**

18410177b Moscow PLASTICHESKIYE MASSY in  
Russian No 3, Mar 89 pp 30-32

[Article by M. D. Fedotova, I. V. Ivankina, N. F. Pilyayeva, G. P. Ivanova, I. G. Kuznetsova]

[Abstract] Studies were made of various types of polyamide-6, with the moisture content monitored in all stages of manufacture of the polyamide products: in granules of the initial polyamide, in granules during drying and before casting, in specimens during storage and immediately before testing in the dry state, and in specimens during moisture conditioning for various periods of time. The mechanical properties were found to depend on moisture content least of all in the granules, most of all in the conditioned finished specimens. Nevertheless, moisture content must be strictly monitored, because it influences the quality of casting and the properties of the products. Figures 2; references 2: 1 Russian, 1 Western.

UDC 678.5.01:66.085.3

**Predicting Properties of Radiation-Modified Polymer Materials**

18410177c Moscow PLASTICHESKIYE MASSY in  
Russian No 3, Mar 89 pp 32-34

[Article by V. I. Dakin, N. A. Shmakova]

[Abstract] The topology of the three-dimensional grids formed during irradiation of polymers determines the operational properties of the modified polymer materials. Increasing the absorbed dose in radiational cross-linking leads first to the formation of branched, soluble macromolecules, then to fragments of a three-dimensional grid (the gel-fraction), and finally to a continuous system of effective grid chains. Prediction of the properties of radiation-modified polymer materials requires investigation of the topology of the grids formed. Predicting the properties by measurement of the modulus of elasticity requires determination of the relationship between the modulus of elasticity and characteristics such as tensile stress, hardness, friction coefficient, durability, heat shrinkage, and diffusion coefficient. A method is developed in this article to predict the properties of radiation-modified plasticized polyvinylchloride. The properties of such materials are thus shown to depend on the structure of the grids formed and can be predicted by measurement of an equilibrium characteristic, such as the modulus of elasticity, which is sensitive to changes in grid topology. Figure 1; references 12 (Russian).



UDC 678.746.222-405.8:539.4

**High-Strength Integral Foam Products Based on Polystyrene***18410177d Moscow PLASTICHESKIYE MASSY in Russian No 3, Mar 89 pp 37-39*

[Article by Yu. T. Panov, A. D. Mitrofanov]

[Abstract] A study is presented of the possibility of decreasing the viscosity of a high-molecular polystyrene melt during the production of foam products equal in strength to pressed foam plastics. The emulsion polystyrene PSE-1 is the focus of the study. The use of temporary plasticizers—low-molecular substances that plasticize the polymer at the processing temperature, but do not affect the properties of the foam products—is found to be quite effective in decreasing viscosity. These products include alcohols whose higher homologs are polystyrene solvents, such as isoamyl and cyclohexanyl alcohols. Low-molecular polystyrene is also an effective plasticizer and, like the alcohols, increases the strength of the foam product. Figures 2; references 4 (Russian).

UDC 678.6.01:677.4:539.2

**Influence of Heat and Mechanical Treatment of Chemical Fibers on Composite Material Properties***18410177e Moscow PLASTICHESKIYE MASSY in Russian No 3, Mar 89 pp 39-42*

[Article by V. V. Andreyeva, M. V. Chibisova, L. A. Kamayevskaya, S. Ye. Artemenko, A. T. Kalashnik]

[Abstract] A study is made of a physical method of modifying fibers that consists of simultaneous exposure to elevated temperature and pressure in order to increase the contact surface and energy of interaction between the surface layer of the fiber and the binder during the creation of composite materials. Studies were performed on polypropylene fiber, capron monofilament and composites based on them; the binder was ED-20 epoxy resin hardened with polyethylene polyamine. The fibers were modified at 5-40 MPa at 293-353 K in a hydraulic press for 10-15 minutes. The transition layer of fiber formed by the treatment produced high flexibility and elasticity in the composite material, indicated by the material's increased elongation at rupture (near that of the fiber itself) and a sharp increase in modulus of toughness. Figures 3; References 10: 9 Russian, 1 Western.

UDC 678.675'126-278:66.067

**Influence of Precipitation Solution on Properties of Microporous Capron Membranes***18410177f Moscow PLASTICHESKIYE MASSY in Russian No 3, Mar 89 p 43*

[Article by T. A. Korshunova, O. A. Mostovlyanskiy, V. A. Artamonov]

[Abstract] A study is made of the properties of microporous capron membranes obtained by the use of precipitation solutions of water + acetone and water + acetic acid with identical precipitation numbers. The results indicate that the chemical nature of the precipitation solution has greatest influence on the deformation and strength properties of the membranes. The structural and filtration characteristics of the membrane are primarily determined by the precipitating capacity of the solutions, not by their composition. References 2 (Russian).

UDC 678.686.01

**Properties of Epoxy Polymers Based on Diglycidyl Diphenylolmethane Esters***18410177g Moscow PLASTICHESKIYE MASSY in Russian No 3, Mar 89 pp 44-47*

[Article by T. A. Kulik, Yu. S. Kochergin, T. I. Koloskova, Yu. M. Paramonov, T. N. Yakub, T. B. Bermas, S. D. Likhobabenko]

[Abstract] A study is made of the properties of polymers based on glycidyl esters of diphenylolmethane (DPM). The initial DPM is a mixture of *o,o'*-, *o,n'*- and *nn'*-isomers. Glycidyl esters of the individual DPM isomers were synthesized by their interaction with epichlorhydrin and subsequent saponification in caustic soda. Superior packing of the structural elements of polymers based on the DPM glycidyl esters, a result of greater kinetic mobility of the fragments of the three-dimensional polymer grid containing the methylene bridge by comparison with the corresponding epoxy diene polymers containing large-volume propylene groups, made for substantial differences in properties such as tensile stress, elongation at rupture, and modulus of toughness. Figure 1; references 6: 5 Russian, 1 Western.

UDC 541.15

**Radiation-Chemical Behavior of  $\text{Np}^{(\text{VI})}$  in Irradiated Tri-N-Butylphosphate**

18410160A Leningrad RADIOKHIMIYA in Russian  
Vol 31 No 1

Jan-Feb 89 (Manuscript received 18 Dec 87) pp 32-36

[Article by M. V. Vladimirova, D. A. Fedoseyev, I. A. Romanovskaya, L. A. Artemova, M. Yu. Gubina]

[Abstract] A spectrophotometric method was used to study the radiation-chemical behavior of  $\text{Np}^{(\text{VI})}$  in gamma-irradiated 30% solutions of TBP in n-dodecane with metal concentration  $2 \times 10^{-2}$  mol/l in the range of absorbed gamma radiation doses of  $1 \times 10^4$  to  $6 \times 10^6$  Gr. The results of investigation of absorption spectra of  $\text{Np}^{(\text{VI})}$ ,  $\text{Np}^{(\text{V})}$  and  $\text{Np}^{(\text{IV})}$  in TBP+n-dodecane demonstrate the possibility of determining the physical-chemical status of these valent forms in irradiated organic solvents. The kinetic behavior of the individual valent forms of neptunium is found to differ from that observed in aqueous solutions. The linear initial sectors of the dose curves indicated the radiation-chemical yields of the complexes with BBPA, indicating that any valent form of neptunium is converted to the 4-valent state variant. Figures 2; References 6: 4 Russian, 2 Western.

UDC 541.17:546.799.4

**Reactivity of Organic Hydrazine Derivatives and Mechanism of Their Reaction with Neptunium and Plutonium Ions**

18410160B Leningrad RADIOKHIMIYA in Russian  
Vol 31 No 1

Jan-Feb 89 (manuscript received 18 Feb 88) pp 55-60

[Article by V. S. Koltunov, S. M. Baranov, T. P. Zharova]

[Abstract] A study of the kinetics of the reaction of reduction of  $\text{Np}^{(\text{VI})}$  to  $\text{Np}^{(\text{V})}$  and of  $\text{Pu}^{(\text{IV})}$  to  $\text{Pu}^{(\text{III})}$  by organic derivatives of hydrazine demonstrated that reactions of this type follow a common mechanism, the differences in reactivity of the individual hydrazine derivatives correlating with changes in basicity of the derivatives and with the induction effect of the organic substituent radical in the hydrazine molecule. Radical substituents with positive induction effect, repelling electrons and increasing the electron density on the nitrogen atom, accelerate the reduction of  $\text{Np}^{(\text{VI})}$  in comparison to unsubstituted hydrazine. Substituents with negative induction effect inhibit this reaction. Figures 2; References 5: Russian.

UDC 546.791.6:546.841

**Coprecipitation of Macroscopic Quantities of Uranium and Thorium in  $\text{UO}_2^{2+}$ - $\text{Th}^{4+}$ - $\text{MO}_3\text{-CO}_3^{2-}(\text{OH})\text{-H}_2\text{O}$  and Investigation of Solid Phases**

18410160C Leningrad RADIOKHIMIYA in Russian  
Vol 31 No 1

Jan-Feb 89 (Manuscript received 11 Apr 88) pp 78-83

[Article by Yu. A. Afanasyev, L. T. Azhipa, A. I. Ryabinin]

[Abstract] The methods of chemical analysis IR spectroscopy, differential thermal analysis and thermogravimetric analysis are used to study solid phases formed upon coprecipitation of uranium (VI) and thorium from carbonate-containing and alkaline solutions. The composition of the solid phases is presented as formulas for the air-dry and calcined phases. Practically complete coprecipitation of uranium and thorium is observed at pH=8.0 from an alkaline solution. In systems with sodium carbonate, the highest relative coprecipitation of uranium and thorium occurs in the system with final pH=5.0. At pH=8.0 in the carbonate medium the thorium coprecipitates less uranium than at other values of pH. Coprecipitation correlates with the content of water and carbonate ions in the precipitates. The higher the atomic-molecular ratio of uranium to  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , the lower the degree of precipitation. Figure 1; References 8: 6 Russian, 2 Western.

UDC 532.739'831.753-532

**Isotope-Pure Berkelium-250 Generator**

18410160D Leningrad RADIOKHIMIYA in Russian  
Vol 31 No 1

Jan-Feb 89 (Manuscript received 12 Feb 88) pp 78-83

[Article by L. I. Guseva, V. V. Stepushkina]

[Abstract] A chromatographic method was developed for permanent isolation of  $^{250}\text{Bk}$ , periodically accumulating in  $^{254}\text{Es}$  on the basis of the isotope generator principle using commonly available cationites and solutions of phosphoric acid as the eluent. A solution containing einsteinium-254 in equilibrium with  $^{250}\text{Bk}$  in any mineral acid except HCl with less than 1 mol/l acid concentration is sorbed on a column filled with a cationite such as dowex-50 in mixture with lead dioxide, which is then washed with a small quantity of water, after which the generator is ready to operate. To extract berkelium, the column is washed with a solution of phosphoric acid at 2-4 mol/l, the berkelium is oxidized to the 4-valent state and washed out in the first portions of eluent, while the einsteinium remains firmly bonded. The method allows periodic isolation of berkelium-250 over the course of two to twelve months. Figure 1; References 6: 1 Russian, 5 Western.



UDC 541.183+546.732+661

**Sodium Titanates as Collectors for Bismuth Radionuclides in Sea Water***18410160E Leningrad RADIOKHIMIYA in Russian**Vol 31 No 1**Jan-Feb 89 (Manuscript received 15 Dec 78) pp 182-35*

[Article by I. V. Melikhov, K. N. Chaliyan, V. M. Komarevskiy, F. A. Belinskaya, L. P. Filina, A. A. Utkin]

[Abstract] A study is made of the sorption of bismuth radionuclides on synthesized sodium titanate specimens with multilevel surface organization. The sorbent was synthesized by a method providing for spontaneous appearance of the hierarchical structure—precipitation of the sorbing phase from strongly supersaturated media. The sorbent was tested using imitation and natural sea water. The results were used to develop a chromatographic method of concentration and determination of short-lived nuclides  $^{212}\text{Bi}$  and  $^{214}\text{Bi}$  in natural sea water. Figure 1, References 8: 6 Russian, 2 Western.

UDC 541.124/128

**Autovibrational and Disorganized Structures in Molecular Gas During Absorption of Modulated Irradiation***18410165a Moscow KHIMICHESKAYA FIZIKA in Russian**Russian**Vol 8 No 3, Mar 89 (manuscript received 11 Apr 88) pp 318-322*

[Article by V. M. Shmelev, N. V. Yevtyukhin, and A. D. Margolin, Institute of Chemical Physics imeni N. N. Semenov, USSR Academy of Sciences, Moscow]

[Abstract] Autovibrational processes in nonequilibrium systems such as those that occur in the laser heating of chemically active media in the absorption of irradiation which affects highly placed vibrational levels of molecules are capturing the interest of researchers. The effect of resonance irradiation that is uniform in space and that has a periodic time component was evaluated as it affected an optically thin gas (CO) layer placed in a reaction vessel. It was observed that, in the range of the threshold cycle during a periodically changing intensity of incoming radiation, a disorganized time structure could appear. It was expressed by an irregular quasiperiodic change in the vibrational and progressive gas temperature. Figures 3; references: 3 (Russian).

UDC 542.91:547.455

**Synthesis of Macrolide Antibiotics. Report 17.  
Synthesis of C<sup>1</sup>-C<sup>10</sup> Fragment of Erythronolides  
(A) and (B)**

18410168j Moscow IZVESTIYA AKADEMII NAUK  
SSSR: SERIYA KHIMICHESKAYA in Russian  
No 3, Mar 89 (manuscript received  
4 Dec 87) pp 680-687

[Article by A. F. Sviridov, V. S. Borodkin, M. S. Yermolenko, D. V. Yashunskiy, Institute of Organic Chemistry imeni N. D. Zelinskiy, USSR Academy of Sciences, Moscow]

[Abstract] A previous report in the same issue of the journal (Sviridov et al., pp 674-680) discussed a strategy for the stereochemically directed synthesis of erythronolides A and B in a linking sequence of (C<sup>5</sup>-C<sup>9</sup>) + C<sup>3</sup>-C<sup>4</sup>) + (C<sup>1</sup>-C<sup>2</sup>) + (C<sup>10</sup>) + (C<sup>11</sup>-C<sup>12</sup>) and described synthesis of the whole C<sup>5</sup>-C<sup>9</sup> fragment. This report discusses synthesis of fragment C<sup>1</sup>-C<sup>10</sup>—a ketone—from the aldehyde synthesized in the previous report and establishes the configuration of the C<sup>3</sup>-C<sup>6</sup> and C<sup>8</sup> centers. References 5: 1 Russian, 4 Western.

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